U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-281 189

Preliminary Environmental Assessment of Energy Conversion Processes for Agricultural and Forest Product Residues. Volume 1

Stanford Research Inst, Menlo Park, Calif.

Prepared for

Municipal Environmental Research Lab, Cincinnati, Ohio

Mar 78

EPA

PB 281 189

United States
Environmental Protection
Agency

Office of
Research and
Development

Municipal Environmental Research
Laboratory
Cincinnati, Ohio 45268

EPA-600/7-78-047
March 1978

PRELIMINARY ENVIRONMENTAL ASSESSMENT OF ENERGY CONVERSION PROCESSES FOR AGRICULTURAL AND FOREST PRODUCT RESIDUES,

Volume I

Interagency
Energy-Environment
Research and Development
Program Report

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NATIONAL TECHNICAL
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U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/7-78-047

2.

3. RECIPIENT'S ACCESSION NO.
PB281189

4. TITLE AND SUBTITLE
PRELIMINARY ENVIRONMENTAL ASSESSMENT OF ENERGY CONVERSION PROCESSES FOR AGRICULTURAL AND FOREST PRODUCT RESIDUES; Volume I

5. REPORT DATE
March 1978 (Issuing Date)

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Benjamin J. Gikis, et al.

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Stanford Research Institute
333 Ravenswood Avenue
Menlo Park, California 94025

10. PROGRAM ELEMENT NO.
EHE624

11. CONTRACT/GRANT NO.
68-01-2940

12. SPONSORING AGENCY NAME AND ADDRESS
Municipal Environmental Research Laboratory--Cin.,OH
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
EPA/600/14

15. SUPPLEMENTARY NOTES
Volume II consists of computer printout data which is not published.
Project Officer: John O. Burckle (513) 684-4491

16. ABSTRACT

A preliminary assessment was made of the environmental impacts of several types of conversion processes for producing energy or fuels from agricultural and forestry residues. Fifteen examples were selected to represent various combinations of agricultural residues and conversion processes available in various geographic regions. The conversion processes included gasification-pyrolysis (Purox), liquefaction-pyrolysis (Tech-Air), combustion (direct firing, both large and small scale), co-combustion with coal, and anaerobic digestion. Residues included animal manure, forestry, and field crops, including sugar cane. Special attention was given to pesticide and herbicide residues in conversion processes. Pesticide residues were found to be generally low in crops and logging wastes and were generally destroyed during thermal processes. While many areas in the United States have high densities of agricultural residues, economic considerations appear to rule out the use of available technologies for obtaining energy from these sources at the present time.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pesticides Residues Contaminants	Solid waste Energy conversion Processes	97F

18. DISTRIBUTION STATEMENT
Not restricted

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
181

22. PRICE
A09 - A01

EPA Form 2220-1 (9-73)

☆ U. S. GOVERNMENT PRINTING OFFICE: 1978-757-140/6806 Region No. 5-II

EPA-600/7-78-047
March 1978

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Volume I

by

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communication link between the researcher and the user community.

With rapidly rising prices for energy, there has been increased interest in obtaining energy from sources other than fossil fuels. The research contained in this report investigated the environmental effects of selected energy conversion processes for utilizing agricultural and forestry residues. The conversion processes included direct combustion, co-firing with coal or lignite, and pyrolysis to produce either gaseous or liquid products. The results will be useful to decision-makers interested in developing future energy sources and maintaining environmental quality.

Francis T. Mayo, Director
Municipal Environmental
Research Laboratory

ABSTRACT

The goal of this project was to determine, in a preliminary study, the environmental impacts of several types of conversion processes that could produce energy or fuels from agricultural and forestry residues.

Fifteen cases were chosen to be representative of the various combinations of agricultural residues and conversion processes available in various geographic regions. Technologies included gasification-pyrolysis (Purox), liquefaction-pyrolysis (Tech-Air), combustion (direct firing both large and small scale), co-combustion with coal (both large and small scale), and anaerobic digestion.

Residues included in the study include manure and forestry, sugar cane field, and field crop residues. Special attention is given to the pesticide and herbicide residues and their ultimate fate in the conversion processes.

Material balances are developed for each case, and special effort is given to include emissions from all sources--including harvesting, transportation, and feed preparation as well as from the conversion process itself. The data generated are compared to expected emissions from coal combustion and coal gasification processes on a net Btu basis to determine the relative environmental impact of the alternatives.

Residue density maps were prepared and utilized in the selection of sites with the highest geographic densities of residues.

This report was submitted in fulfillment of Contract No. 68-01-2940 by Stanford Research Institute International under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period June 12, 1976, to April 30, 1977, when work was completed.

CONTENTS

Foreword iii
Abstract iv
Figures vii
Tables viii
Conversion Units xii

1. Introduction 1
2. Conclusions 2
3. Recommendations 6
4. Process and Site Selection Data 7
5. Residue Data 10
6. Pesticide Data 20
   - Pesticide usage 20
   - Pesticides and herbicides used on sugarcane in Florida 27
   - Pesticides used on cattle manure in Colorado 29
   - Pesticides and herbicides used on wheat in Colorado 32
   - Pesticide and heavy metal residue in chicken manure in Arkansas 33
   - Pesticide used in forestry applications in the United States . 35
   - Pesticides and herbicides used on field crops 36
7. Collection and Transportation 38
   - Forestry residue 38
   - Sugarcane trash 39
   - Transportation of crop residue to power plants 41
   - Manure 41
8. Anaerobic Digestion 43
   - Locations 43
   - Process description 43
   - Environmental analysis 50
   - Potential process problems 53
9. Direct Firing of Residue 57
   - Introduction 57
   - Process description 57
   - Process feeds 57
   - Land disruption from conversion process 58
   - Direct combustion of forestry residue 59
   - Direct combustion of sugarcane residue 62
   - Cofiring with coal in a stoker-fired boiler 66
10. Large-Scale Cofiring with Coal 76
   - Cofiring of forestry wastes with coal 76
   - Cofiring of sugarcane field wastes with coal in large utility boilers 76

11. Pyrolysis Technology 78
  Introduction 78
  Processes 81
  Process feeds 82
  Tech-air with wood residue 85
  Purox* with wood residue 102
  Tech-air with rice and cotton wastes 111
  Purox* with rice waste 112
  Purox* with barley and cotton waste 121

References 129

Appendices

A. Anaerobic digestion - supplemental data 132
B. Environmental analysis assumptions, calculations, and data summary 151
C. Data comparison for bio-gas, CRAP, and SRI model cases 162

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*Registered trademark

FIGURES

Number		Page
1	Density of manure residue	12
2	Density of logging residue	14
3	Density of crop residue	16
4	Density of total residue	18
5	Pathways for the methane fermentation of complex wastes	44
6	Anaerobic process for manure digestion	46
7	Sample plot plan showing 32 digesting tanks	47
8	Energy production and consumption of anaerobic digestion process using various agricultural wastes as digester feed	48
9	Simplified material balances	49
10	Material balance	51
11	Land requirements	54
12	Input water requirements	54
13	NO_x emissions	55
14	SO_2 emissions	55
15	Particulate emissions	56
16	Solid wastes	56
17	Direct firing of sugarcane trash	62
18	Cofiring with coal in a stoker-fired boiler	67
19	Georgia Tech pyrolysis process	87
20	Purox* process	103
C-1	CRAP system mass balance	162
C-2	Bio-Gas Inc. system mass balance	163

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TABLES

Number | Page

1 Environmental Impact 3

2 Sites and Processes 8

3 Conversion Technology 9

4 Physical Properties of Pesticides Applied to Cotton and Barley in California 22

5 Physical Properties of Pesticides Applied to Cotton in Mississippi 26

6 Sugarcane Pesticides 28

7 Pesticides Used for Fly Control in Cattle Feedlots 29

8 Mist Spray Calculation 31

9 Pesticides and Herbicides Applied to Wheat in Colorado 32

10 Fly Sprays and Application Rates 34

11 Forest Area Aerially Sprayed with Insecticides in the U.S. 36

12 Estimated Emissions from Equipment Used to Transport Cane Trash 41

13 Emission from Equipment Used to Transport Residue 42

14 Quantities of Waste Material Used in Anaerobic Digestion 45

15 Precipitation and Evaporation Rates 52

16 Sample Environmental Analysis Worksheet 52

17 Material Balance 60

18 Environmental Impacts of Direct Combustion of Logging Residue, Humboldt County, California 61

Number Page

19 Material Balance for Sugarcane Trash Combustion 63

20 Environmental Impacts, Direct Combustion of Sugarcane Trash 64

21 Material Balance 72

22 Emissions 72

23 Energy Balance 73

24 Energy Consumption and Particulate Emission for Dryer 73

25 Material Balance Output 74

26 Land Usage for Crop Residue 75

27 Comparison of Air Emission 77

28 Pyrolysis and Gasification Reactions 79

29 Approximate Analysis of All Other Components 83

30 Assumed Analysis of Rice Hulls and Straw 83

31 Assumed Analyses of Barley Straw and Cotton Mixed Waste Feed (Moisture Free Basis) 86

32 Tech-Air Pyrolysis Process Stream Flows 88

33 Fuel for Wood Drying 90

34 Diesel Engine Emissions 94

35 Analysis of Dryer Stack Effluents 95

36 Environmental Impacts of Tech-Air Pyrolysis of Wood Residue 96

37 Compounds Formed by Wood Carbonization 97

38 Compounds Reported to be Present in Hardwood Smoke 99

39 Comparison of Wood Residue and Refuse Composition 104

40 Purox® Product Gas Analysis (from Wood Residue Feed) 104

41 Disposition of Minor Constituents in Wood Residue Fed to Purox® Process 105

Number Page

42 Environmental Impact of Purox® Pyrolysis of Wood Residue 109

43 Estimated Disposition of Trace Elements in Wood Residues Fed to Purox® System 110

44 Comparisons of Rice Waste and Refuse Composition 112

45 Assumed Offgas Composition from Rice Waste Pyrolysis via Purox® Process 113

46 Purox® Process Stream Flows Using Rice Waste Feed 114

47 Minor Elements Reported Present in Rice Hulls 115

48 Sensible Heat Requirements 116

49 Environmental Impacts of Purox® Pyrolysis of Rice Waste 120

50 Comparisons of Barley/Cotton Waste and Refuse Compositions 121

51 Assumed Offgas Composition from Barley/Cotton Waste Pyrolysis via Purox® Process 122

52 Purox® Process Stream Flows Using Barley and Cotton Waste as Feed 123

53 Environmental Impacts of Purox® Pyrolysis of Barley and Cotton Waste 128

A-1 Waste Characteristics 140

A-2 Summary of Assumptions for Determining f_v, G, and f_d 141

A-3 Material Balance for Fresh Cattle Manure as Digester Feed with Liquid Recycling 144

A-4 Material Balance for Five-Month-Old Cattle Manure as Digester Feed with Liquid Recycling 145

A-5 Material Balance for Fresh Manure and Wheat Residue as Digester Feed with Liquid Recycling 146

A-6 Material Balance for Chicken Manure as Digester Feed Without Liquid Recycling 147

A-7 Material Balance for Chicken Manure as Digester Feed with Liquid Recycling 148

Number Page

A-8 Sulfur and Nitrogen Emission per 10^6 Btu Net Supply Production for Anaerobic Digestion Process 149

A-9 Sulfur and Nitrogen Emission Per Day for Anaerobic Digestion Process 150

B-1 Coal-Fired Power Plant Emissions to Air 151

B-2 Water Requirements for Coal-Fired Power Plant 152

B-3 Coal-Fired Power Plant System Emissions and Land Disturbance . . . 153

B-4 Coal Combustion for Electric Power Generation 154

B-5 Coal Gasification with Lurgi Technology 155

B-6 Water Requirements for Coal Gasification Using Lurgi Technology 155

B-7 Lurgi Coal Gasification Plant Emissions and Land Disturbances . . . 156

B-8 Coal Gasification 157

B-9 Anaerobic Digestion 158

B-10 Anaerobic Digestion 159

B-11 Anaerobic Digestion 160

B-12 Anaerobic Digestion 161

C-1 Comparison of Parameters Used by Bio-Gas, Inc. and SRI for Cattle Manure 164

C-2 Comparison of Selected Parameters for Bio-Gas, Inc., CRAP, and SRI Model Cases 165

CONVERSION UNITS

Some English units that are still in common use are employed in this report. The following table lists the factors to be used to convert English units to metric.

Multiply English unit	By conversion	To obtain metric unit
acres	0.405	hectares
acre-feet	1233.5	cubic meters
barrel, oil	158.97	liters
British thermal unit	0.252	kilogram-calories
British thermal unit/ pound	0.555	kilogram calories/kilogram
cubic feet/minute	0.028	cubic meters/minute
cubic feet/second	1.7	cubic meters/minute
cubic feet	0.028	cubic meters
cubic feet	28.32	liters
cubic inches	16.39	cubic centimeters
degree Fahrenheit	0.555(°F - 32)[a]	degree Celsius
feet	0.3048	meters
gallon	3.785	liters
gallon/minute	0.0631	liters/second
horsepower	0.7457	kilowatts
inches	2.54	centimeters
inches of mercury	0.03342	atmospheres
pounds	0.454	kilograms
million gallons/day	3785	cubic meters/day
mile	1.609	kilometer
pound/square inch (gauge)	(0.06805 psig + 1)[a]	atmospheres (absolute)
square feet	0.0929	square meters
square inches	6.452	square centimeters
tons (short)	0.907	metric tons (1000 kilograms)
yard	0.9144	meters

[a] Actual conversion, not a multiplier.

SECTION 1

INTRODUCTION

As a result of the energy crisis and the dwindling reserves of conventional fossil fuels, much attention has been focused on the use of waste materials and byproducts as sources of energy. Renewable resources such as agricultural crop wastes, forestry wastes, and cattle manure are all potential sources of energy and chemical feedstocks. To date, investigations have considered the technical and economic problems -- that is, how much feedstock is available at what cost, and what are the costs and technical problems associated with processing the waste? However, little attention has been given to the environmental effects of using these agricultural reidues as energy sources.

This study seeks to fill that need by assessing the environmental effects of several energy conversion processes that use agricultural residue, forestry residue, or manure as feedstocks. The conversion processes include direct combustion, cofiring with coal or lignite (on both a large and small scale), and pyrolysis to produce either gaseous or liquid products.

This study addresses waste availability and emissions from transportation, pesticide and herbicide residue, and the conversion processes themselves. The economics of the processes are not a main focus of this project, although site locations and process selections were based on those combinations that appear to have the most favorable economics. Conducting an environmental assessment study of energy systems (including fuel extraction or production, fuel preprocessing and transport, energy conversion, energy transport, and end use) is difficult, however, without making a concurrent economic analysis. This lack of an economic analysis is most severe in the energy conversion portion. While one can compare the uncontrolled emission from the basic processing units, the specific contaminant emissions per ton of material processed or per unit of energy production can, almost without exception, be controlled to comparable levels for all conversion processes. This control is strictly a question of cost.

One approach to comparing conversion processes on a common basis is to specify that emissions are compared for conversion plants producing an energy product for $X/10^6$ Btu and with capital investment costs ranging from \$Y to $Z/10^6$ Btu of daily capacity. Another approach is to specify the emission levels and then to estimate the cost to achieve these levels. Neither approach was within the scope of this project.

SECTION 2

CONCLUSIONS

In this preliminary analysis, we have compared the relative environmental effects of agricultural residue conversion systems with the most likely alternative sources of energy -- that is, gas- or oil-producing systems (such as pyrolysis or anaerobic digestion) are compared with a gas-producing process, namely, coal gasification. Direct combustion of residue is compared with direct combustion of coal under favorable circumstances (mine-mouth power plant burning low-sulfur coal). Cofiring is compared with the firing of 100% fossil fuel at the same location. Hence, crop residue cofired with lignite in North Dakota is compared to the firing of lignite only at the same location. This technique allows an assessment of the relative effects of using the agricultural residues.

The format is similar to that of the Council on Environmental Quality in that all effects are considered from resource extraction through the conversion plant. Because the energy output from a coal conversion plant and an agricultural residue processing plant differs, the results are compared on the basis of units per million Btus produced. In calculating the net energy produced from gas-producing processes, we have assumed that purchased electric power is generated by coal-fired power plants with no transmission losses and a plant thermal efficiency of 40%. In calculating the net outputs a figure equal to the Btu equivalent of the fuel burned to produce the electric power is subtracted from the energy output of the coal gasification and the residue processing systems. The pollutants generated in the production of electric power for use at the gas-producing facilities are shown on the emissions comparison tables, along with the emissions of the gas-producing facilities.

The standard of comparison for a coal-fired power plant is a new mine-mouth power plant burning 0.8% sulfur coal and using flue gas desulfurization to reduce SO_2 emissions to 0.83 $lb/10^6$ Btu. The cofiring standard of comparison uses locally available coal or lignite and does not use flue gas desulfurization and particulate data presented for cases with and without control measures.

The environmental impact data are summarized in Table 1. One important point to note is that no wastewater need be discharged in areas with high net evaporation rates. Purox® pyrolysis technology for Humboldt County, California, and direct firing or cofiring processes to be located in Florida, Alabama, Missouri, and Iowa may not be able to use evaporation ponds. In all other cases, the wastewater is sent to evaporation ponds. This reflects

TABLE 1. ENVIRONMENTAL IMPACT

Case	Acres/ 10^9/Btu/yr	Water input[a] (gal/10^6 Btu)	Waste water output (gal/10^6 Btu)	Air Emissions						Solid waste
				NO_x[b]	SO_2[c]	H_2S	Particulates[d]	CO	Hydrocarbons	
				(lb/10^6 Btu)						
Gas- and Oil-Producing Processes										
Coal gasification - comparison case (with environmental controls)	0.014	28	6.9	0.007	0.1004	0	0.052			47
Anaerobic digestion										
Cattle manure - Weld Co., Colorado	0.25	187	0	0.161	0.18	0	0			0
Cattle manure and wheat residue - Weld Co., Colorado	0.113	0	0	0.171	0.148	0	0			0
Chicken manure - Washington Co., Arkansas	0.116	626	0	0.187	0.90	0	0			0
Pyrolysis - Purox®										
Wood - Humboldt Co., California	<0.01	1.25	3.17	0.12	0	0	0			1.6
Rice - Cutter Co., California	0.08	0.7	5.4	0.014	0.02	0	0.004			34.7
Cotton and barley - Kern Co., California	0.03	0.6	3.6	0.026	0.016	0	0.003			10.6
Pyrolysis - Tech-Air										
Wood - Humboldt Co., California	<0.01	0.57	0	0.12	0	0	0			0
Cotton and rice - Bolivar Co., Mississippi	N/A	N/A	N/A	N/A	N/A	N/A	N/A			N/A
Power-Direct Combustion										
Coal combustion - comparison case, mine-mouth power plant, low sulfur coal	0.085	208	8	2.0	0.83	0	0.14			54
Direct firing										
Wood - Humboldt Co., California	0.001	175	0	0.7	0.0	0	0.1 (8-10)	0.25	0.25	0.7
Sugarcane residue - Hendry, Florida	0.011	175	0	0.62	0.0-0.1	0	0.62 (6.8)	0.62	0.62	6.6
Power - Cofiring										
Large scale										
Wood and coal (25/75) - Green Co., Alabama	<0.05	208	8	1.0	4.3	0	0.3-0.4 (10-14)	0.14	0.10	23.7
Coal only - Green Co., Alabama		208	8	0.4-0.6	5.7	0	0.16 (8.2)	0.06	0.015	31.0
Sugarcane and coal (25/75) - Hendry, Florida	<0.05	208	8	0.6	4.3	0	0.2-0.4 (7)	0.27	0.15-0.17	24.9
Coal only - Hendry, Florida		208	8	0.4-0.6	5.7	0	0.16 (8.2)	0.06	0.015	31.0
Small scale										
Crops and lignite (25/75) - Traill, N.D.	<0.05	208	8	1.4	1.7	0	0.34 (2.17)	0.57	0.20	39.7
Lignite only - Traill, North Dakota	<0.05	208	8	1.4	2.1	0	0.32 (2.4)	0.48	0.23	45.5
Crops and coal (25/75) - Marshall, Mo.	<0.05	208	8	4.3	2.4	0	0.42 (3.4)	0.37	0.059	28.1
Coal only - Marshall, Missouri	<0.05	208	8	4.3	3.1	0	0.39 (3.0)	0.14	0.043	30.6
Crops and coal (25/75) - Sibley, Iowa	<0.05	208	8	2.2	2.5	0	0.49 (3.2)	0.54	0.21	29.0
Coal only - Sibley, Iowa	<0.05	208	8	2.2	3.2	0	0.41 (3.05)	0.30	0.15	31.0

[a] Includes water for stack gas scrubber where applicable.

[b] NO_x values uncertain.

[c] Uncontrolled.

[d] Without controls in parentheses.

the anticipated planning of the process designs to avoid wastewater discharge in excess of EPA standards. Actual wastewater generated by these processes is quite low (a maximum of 8 gal/10^6 Btu output)*, which again reflects proper process design to eliminate unnecessary wastewater discharge and to achieve minimum water usage.

The data compare favorably with the coal combustion and coal gasification standards of comparisons. In most cases, NO_x emissions are lower in coal combustion, and SO_2 emissions are lower when low-sulfur feedstock is used exclusively. In cofiring, local coals are assumed as feedstocks and the potential emission of SO_2 is quite high, thus requiring flue gas desulfurization to meet environmental standards. Solid wastes are lower, and no hard evidence is indicated of pesticide residue reentering the environment in significant quantities. Since particulate emission tends to rise in most cases of residue combustion, proper attention to particulate removal must be given by the design engineers.

The following conclusions can be drawn from this study:

1. Organic pesticide residues found in crops are generally destroyed in thermal processes, although some volatile compounds may be distilled in the drying steps.
2. Pesticide residue is generally very low for crop and logging residue.
3. Heavy metals (such as arsenic) are used in chickenfeed supplements and cotton crops; these metals could present a serious process and environmental problem.
4. Many sites in the United States have a high density of agricultural residues making conversion processes more likely to be economically feasible. However, economics generally prevent use of the technologies. In cases where a disposal cost is associated with a residue (such as manure), the conversion processes may be economically attractive.
5. Many highly carcinogenic compounds are found in pyrolysis oils, such as the oil produced by the Tech-Air process.
6. Data are sparse on the combustion of agricultural residue in boilers; no data exist on the cofiring of agricultural or forestry residue in coal.
7. Some data indicate that removal of crop residue and forestry residue (especially stumps) is detrimental to the soil condition and that fertilizer is needed to replace the nutrients of the material removed. Also, the removal of stumps in forests may increase erosion. However, other data indicate that the removal of residue helps control rodents, insects, and crop disease.

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*English measurements were the primary units of measure used during the preparation of this study. For the convenience of the reader, a table converting the units of measure to the metric system can be found immediately preceding Section 1.

8. The technologies discussed in this report are in various stages of development. For instance, wood combustion has been practiced for years; several wood-fired boilers are in operation. Conversion of forestry residue may present some problems, however. Other technologies, such as Purox®, have not yet been demonstrated on agricultural residue.

9. It is difficult to accurately predict soil inclusion in agricultural residues without specifying the harvesting technique as well as the weather and soil condition at the time of harvest. Herbicide residues in the soil which may be collected along with the agricultural residues may present environmental problems resulting from the collection and conversion processes.

10. In some combustion processes, the production of high-resistivity fly ash could complicate the efficient operation of electrostatic precipitators.

11. In general, it may be stated that solid waste disposal problems are alleviated by the technologies being studied. However, because of the differences in the basic processes and feedstocks considered and used for residues, it is difficult to draw any firm conclusions concerning the relative solid waste impacts.

SECTION 3

RECOMMENDATIONS

Since this study is a preliminary assessment of environmental problems associated with the use of agricultural residue, the main purpose is to identify areas where potential environmental problems exist and where data are needed. Recommendations for further work include a study of the process economics and the specific environmental areas where data are lacking. Specifically, in the areas of direct firing and cofiring of residue, data are sparse. A complete emissions inventory on a specific proposed process is needed, since the emissions may vary greatly from process to process, even though the technologies are similar. Similarly, little data exist on the nitrogen oxide emissions for these conversion processes. Particulate emissions and control techniques are also difficult to estimate, as they depend highly on the configuration and operating parameters of the combustion processes.

Detailed studies are needed on the inclusion of herbicides and heavy metals in agricultural residue and their end products in the processes. Again, many variables are involved and a specific case must be evaluated that includes specified collection, feed preparation, and conversion technologies.

To date, the Purox® process has not been demonstrated on agricultural residue. Such a demonstration, with associated emissions data collection, might be the most economical way to evaluate the process and collect the required data.

Consideration should be given to the effect that removing residue from the fields and forests has on the nutrient concentrations in the soil and on erosion. Such a study is beyond the scope of this report.

Cofiring technology needs a study of the problems associated with feed preparation and the handling of residue. Equipment design and operating economics need to be determined and the overall effect on emissions must be calculated.

As further specific technologies are proposed, they should be evaluated in a preliminary manner. In this study, only a limited number of cases could be considered.

SECTION 4

PROCESS AND SITE SELECTION DATA

The specific processes and sites evaluated in this project were selected at the outset of the project through discussions between Stanford Research Institute (SRI) and the Environmental Protection Agency (EPA). The six processes assigned by EPA included two pyrolysis processes (Purox® and Tech-Air), anaerobic digestion, direct firing, large-scale cofiring, and small-scale cofiring. After reviewing the waste inventory data, 15 cases were selected. These cases represented at least two of each process, and a total of 11 different locations. Table 2 shows the residue type and the conversion technologies chosen. The numbers correspond to the specific case numbers in Table 3. The process and site selection were based on availability of large quantities of residue and on the suitability of the specific process to handle the given feedstock. Those feedstocks (residue) that are disposal problems or that are of little commercial value were given high priority.

TABLE 2. SITES AND PROCESSES

Case No.	Location	Residue	Process
1	Humboldt County, California	Forestry residue	Large-scale pyrolysis (Purox®)
2	Humboldt County, California	Forestry residue	Small-scale pyrolysis (Tech-Air)
3	Humboldt County, California	Forestry residue	Direct firing in large utility boiler
4	Green County, Alabama	Forestry residue	Cofiring with coal in large utility power plant
5	Weld County, Colorado	Cattle manure	Anaerobic digestion
6	Weld County, Colorado	Cattle manure mixed with wheat residue	Anaerobic digestion
7	Washington County, Arkansas	Chicken manure	Anaerobic digestion
8	Sutter, Butte and Colusa Counties, California	Rice hulls and rice straw	Large-scale pyrolysis (Purox®)
9	Kern County, California	Cotton field waste, cotton gin waste, and barley straw	Large-scale pyrolysis (Purox®)
10	Bolivar County, Mississippi	Cotton gin waste, cotton field waste, rice hulls, rice straw	Small-scale pyrolysis (Tech-Air)
11	Hendry and Palm Beach, Florida	Sugarcane tops and leaves	Direct combustion
12	Hendry and Palm Beach, Florida	Sugarcane tops and leaves	Large-scale cofiring with coal
13	Traill, North Dakota and surrounding counties	Barley, wheat and sunflower residue	Small-scale cofiring with lignite in a stoker-fired boiler
14	Marshall, Missouri and surrounding counties	Wheat and field corn waste	Small-scale cofiring with coal in a stoker-fired boiler
15	Sibley, Iowa and surrounding counties	Field corn residue	Small-scale cofiring with coal in a stoker-fired boiler

TABLE 3. CONVERSION TECHNOLOGY

Residue	Anaerobic digestion	Large-scale pyrolysis (Purox®)	Small-scale pyrolysis (Tech-Air)	Direct firing	Large-scale cofiring with coal (St. Louis)	Small-scale cofiring with coal (Battelle)
Forestry residue		1	2	3	4	
Cattle manure	5					
Cattle manure and wheat	6					
Chicken manure	7					
Cotton field and cotton gin waste Cotton field and cotton gin waste plus barley waste			9			
Rice straw and rice hulls		8				
Rice straw and hulls plus cotton field plus cotton gin waste			10			
Sugarcane waste				11	12	
Wheat, barley, sunflower						13
Wheat and field corn						14
Corn						15

SECTION 5

RESIDUE DATA

This section contains the residue density maps (Figures 1 through 4) prepared from the computer printout of the data in volume 2. The four residue categories presented are: crop residue, forestry (logging) residue, livestock (manure) residue, and total residue. The basic data for this study was taken from the National Science Foundation Data Bank of Agricultural Residues (prepared by Stanford Research Institute under Grant No. AER74-18615 A03-NSF/RANN/SE/GI/18615/FR/76/3), which lists residue by state and county. In this study, the data are grouped by agricultural regions within the states. Each region is an area of similar agricultural activity having a radius of approximately 50 miles. Generally, each region incorporates more than one county.

The data represent only the available residue, those that are realistically retrievable. Also, the data are corrected for moisture and are presented on the basis of dry tons per year. The livestock (manure) data are based entirely on confined feeding (feedlot). Logging residue includes those residues left in the forest during logging operations as well as mill residue at primary wood product plants (wood and bark). Crop residue estimates are based on residue factors developed for each crop (amount of residue per ton of product). These factors were applied to production data during 1971-1973 to generate average annual quantities. Hay and forage crops are specifically excluded.

The data are reported both as total dry tons by region and as a density (dry tons per square mile). The crop residue, logging residue, and total residue data are presented on the map as dry tons per square mile. The manure data are presented slightly differently. Since the manure is from a totally confined feeding operation (feedlots) the per-square-mile approach is not meaningful. The more useful number is total dry tons per year, and the numbers are presented in this way.

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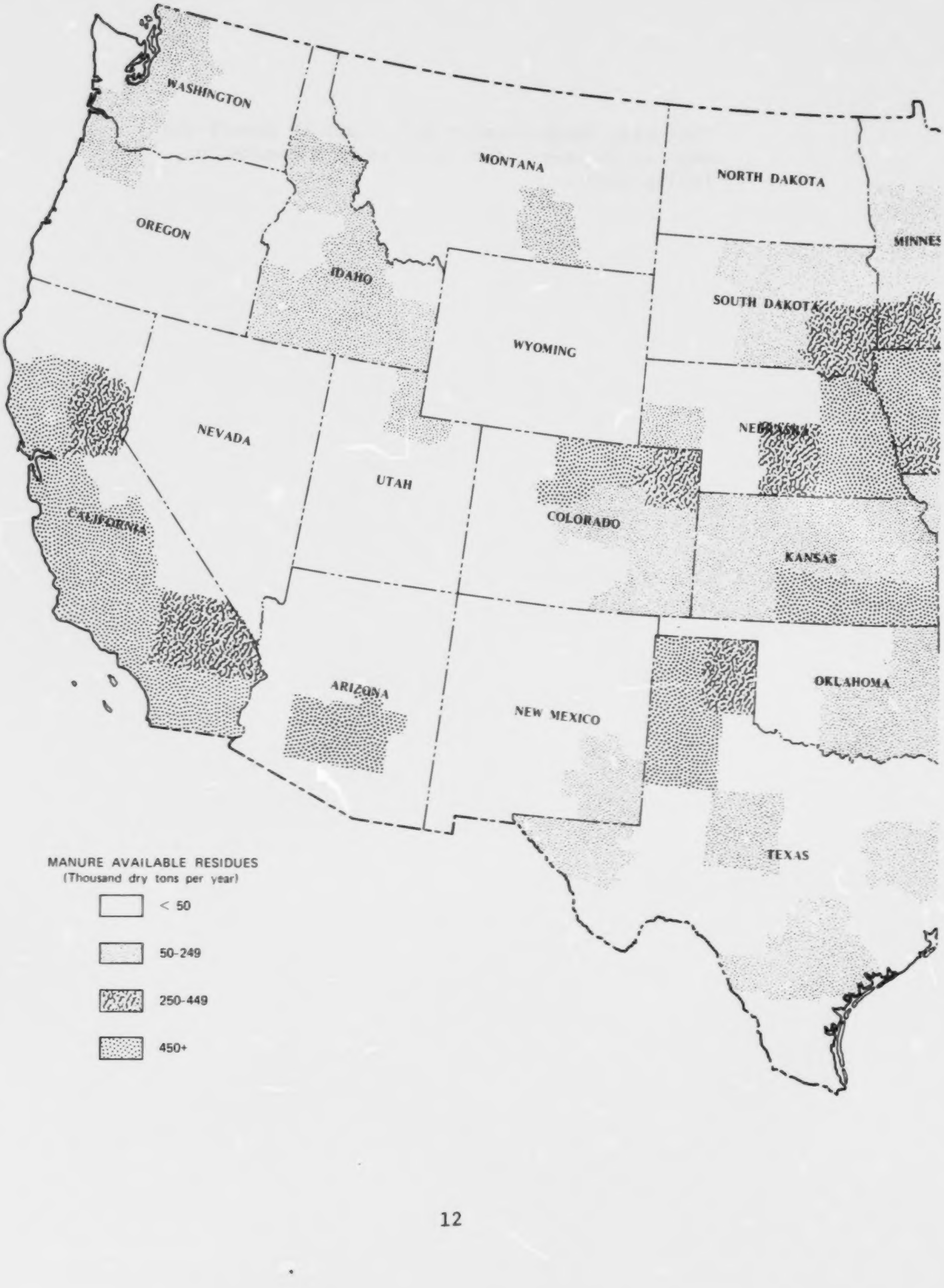
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MONTANA
NORTH DAKOTA
OREGON
IDAHO
MINNES
SOUTH DAKOTA
WYOMING
NEVADA
NEBRASKA
UTAH
CALIFORNIA
COLORADO
KANSAS
ARIZONA
NEW MEXICO
OKLAHOMA
TEXAS
MANURE AVAILABLE RESIDUES
(Thousand dry tons per year)
< 50
50-249
250-449
450+

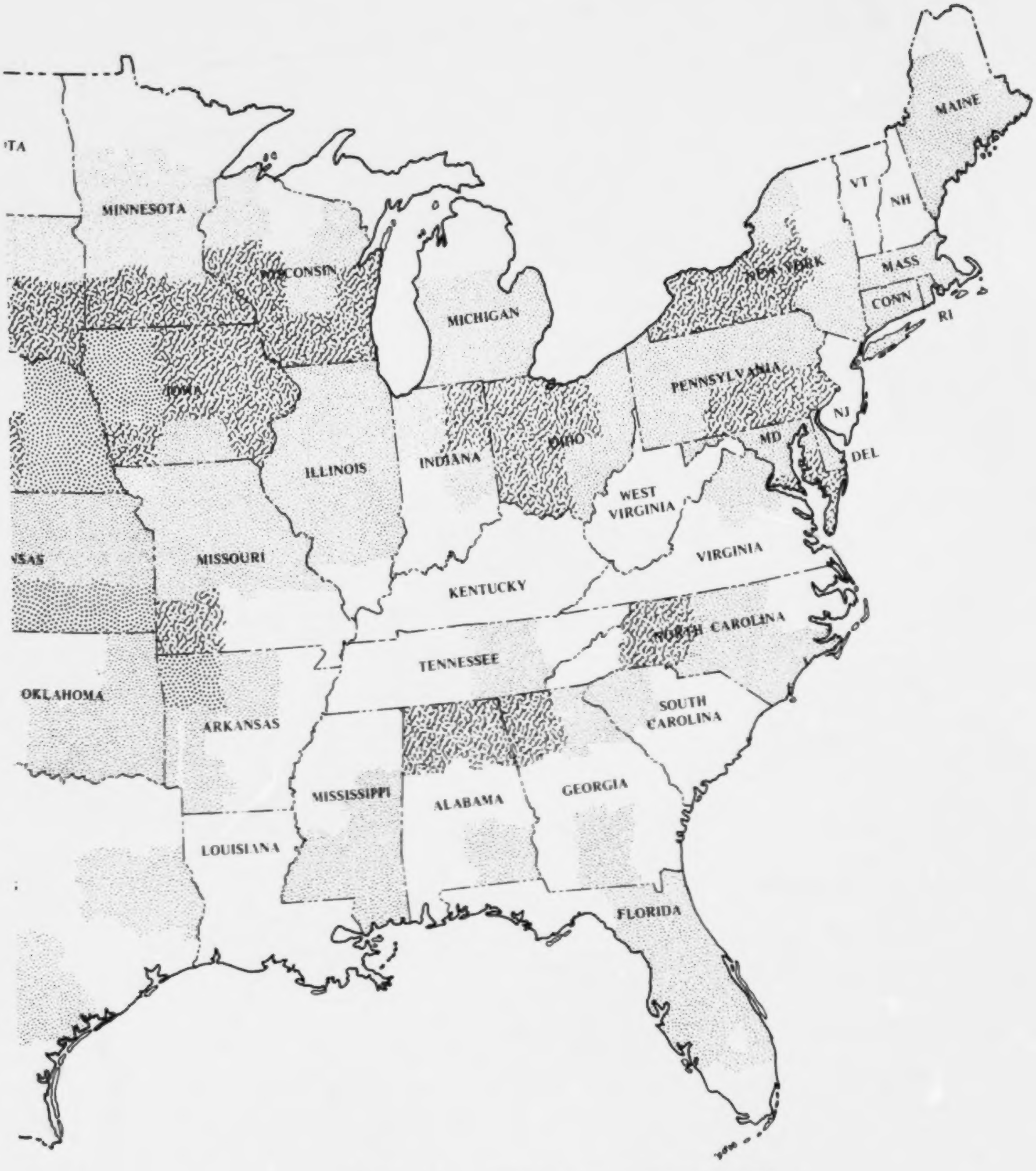
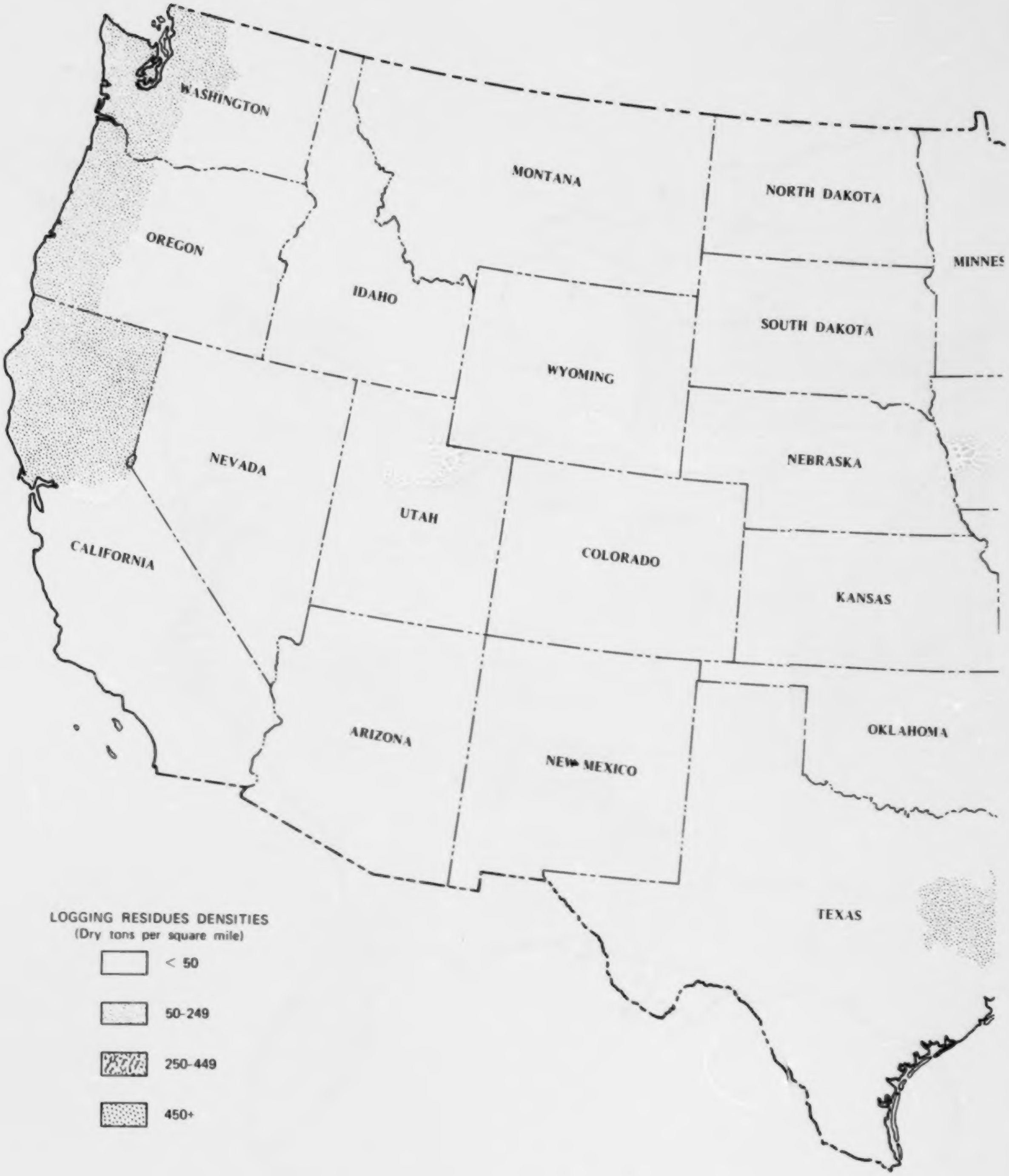


Figure 1. Density of manure residue.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UTAH
COLORADO
CALIFORNIA
KANSAS
ARIZONA
NEW MEXICO
OKLAHOMA
TEXAS
LOGGING RESIDUES DENSITIES
(Dry tons per square mile)
< 50
50-249
250-449
450+

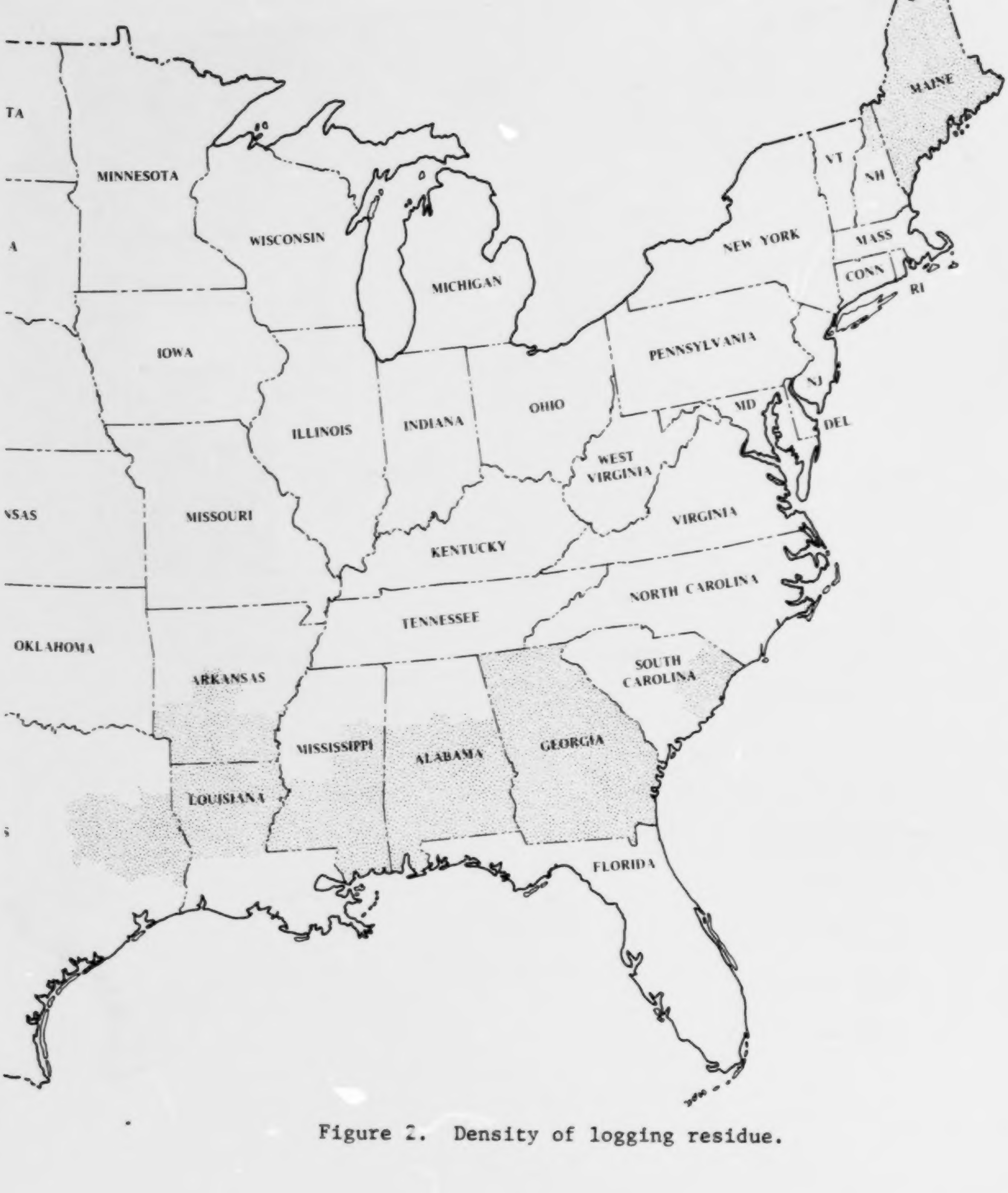
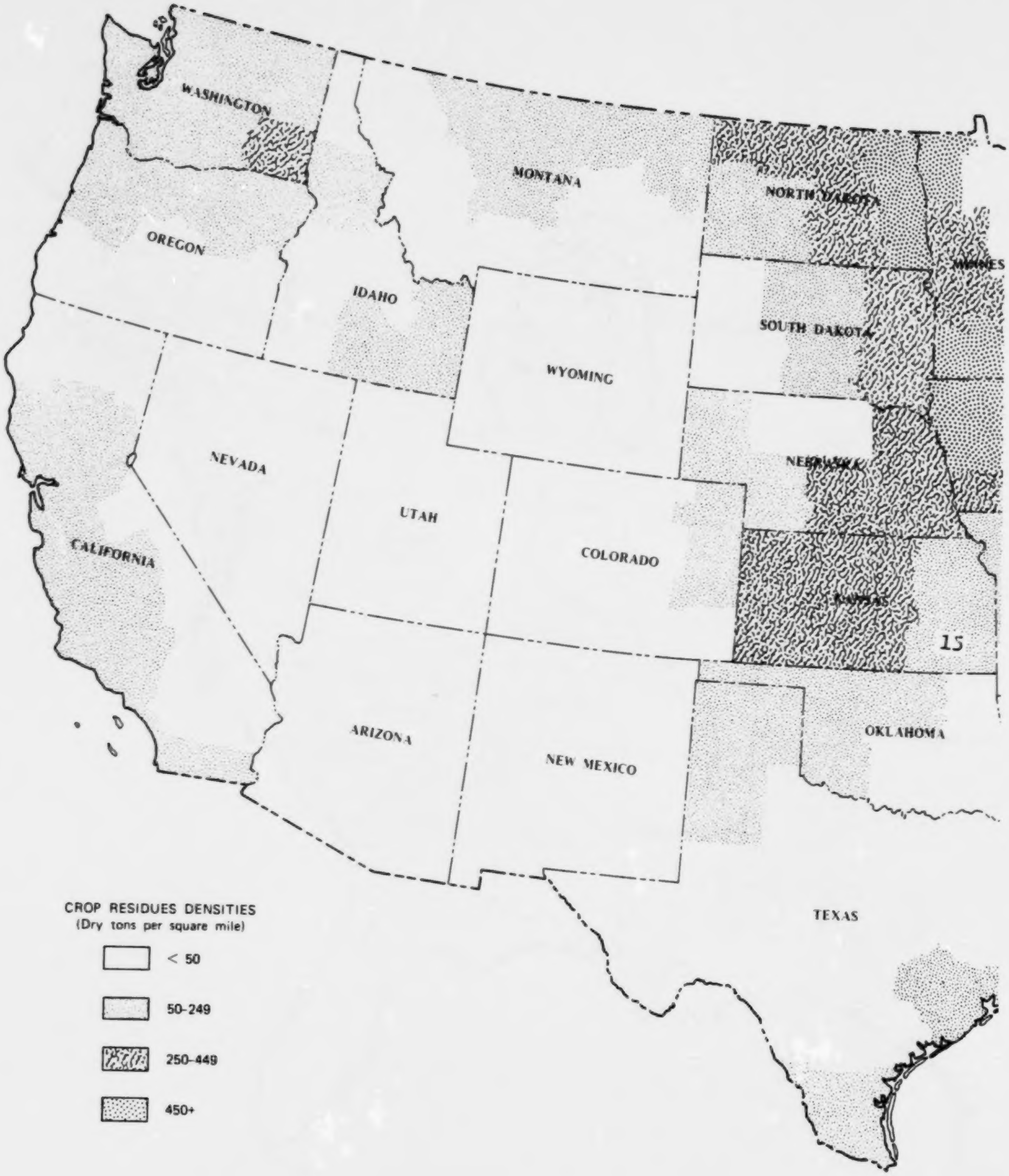


Figure 2. Density of logging residue.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UTAH
CALIFORNIA
COLORADO
KANSAS
15
ARIZONA
NEW MEXICO
OKLAHOMA
TEXAS
CROP RESIDUES DENSITIES
(Dry tons per square mile)
< 50
50-249
250-449
450+

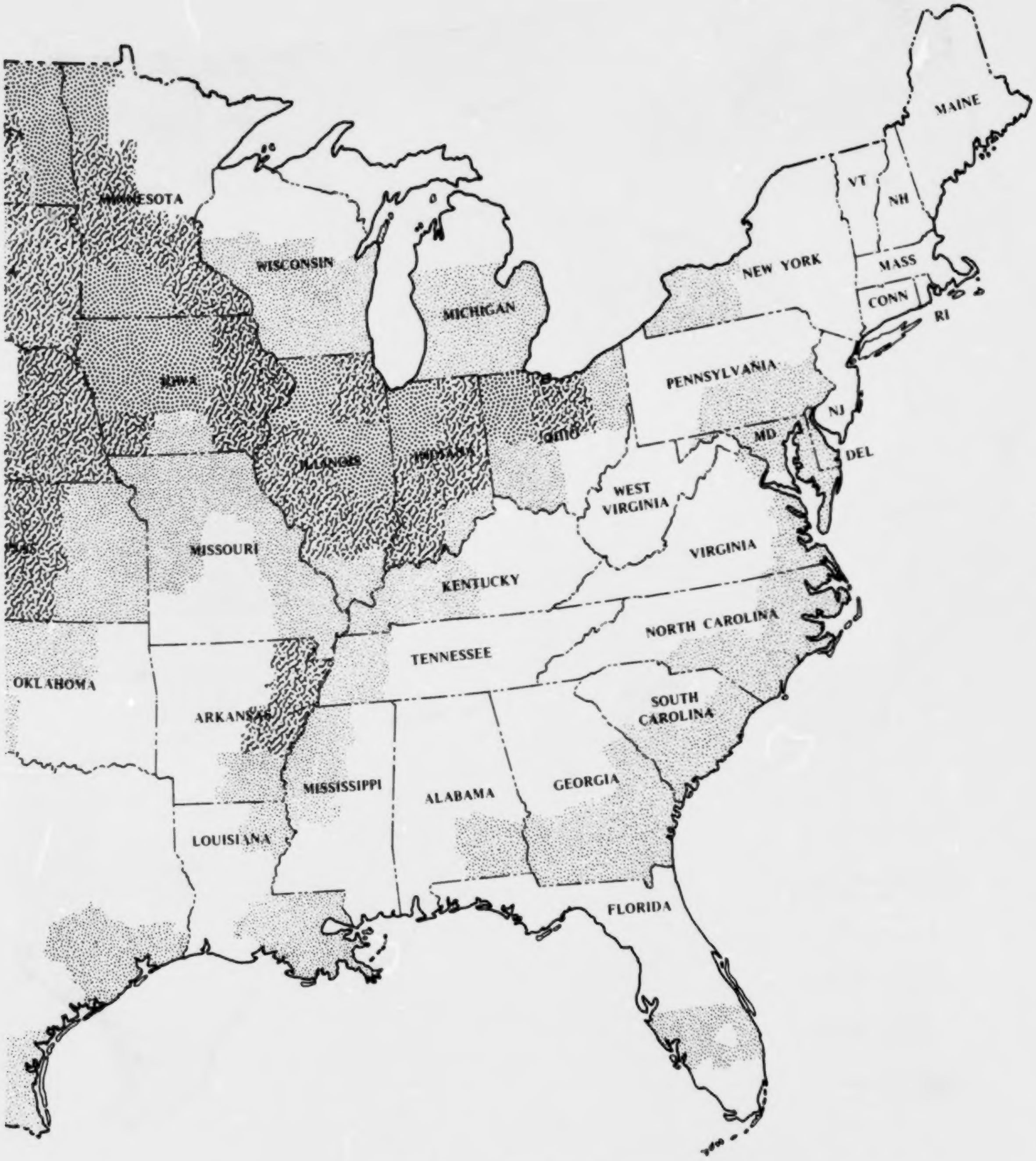
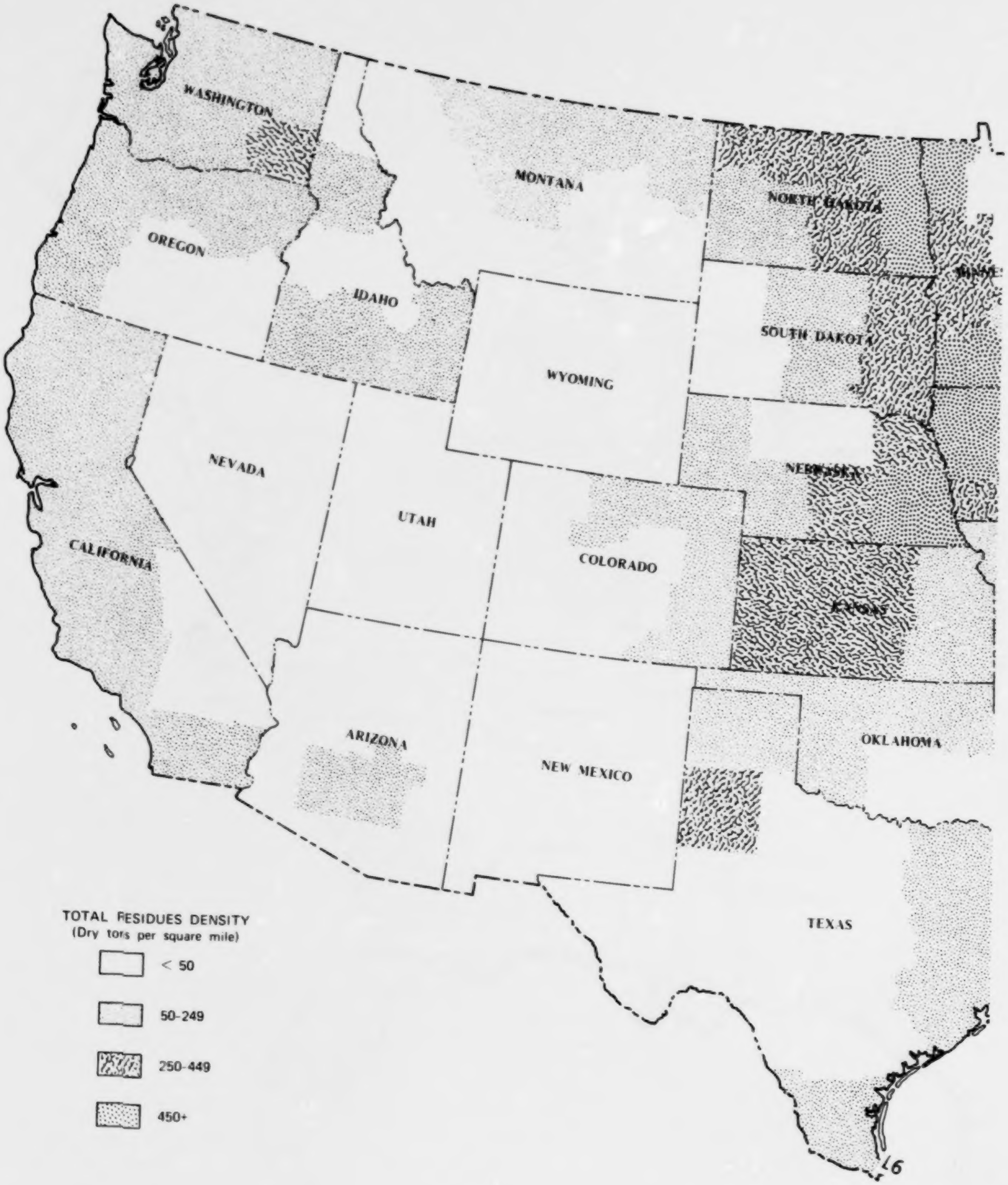


Figure 3. Density of crop residue.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NEVADA
UTAH
COLORADO
CALIFORNIA
KANSAS
ARIZONA
NEW MEXICO
OKLAHOMA
TEXAS
TOTAL RESIDUES DENSITY
(Dry tons per square mile)
< 50
50-249
250-449
450+
16

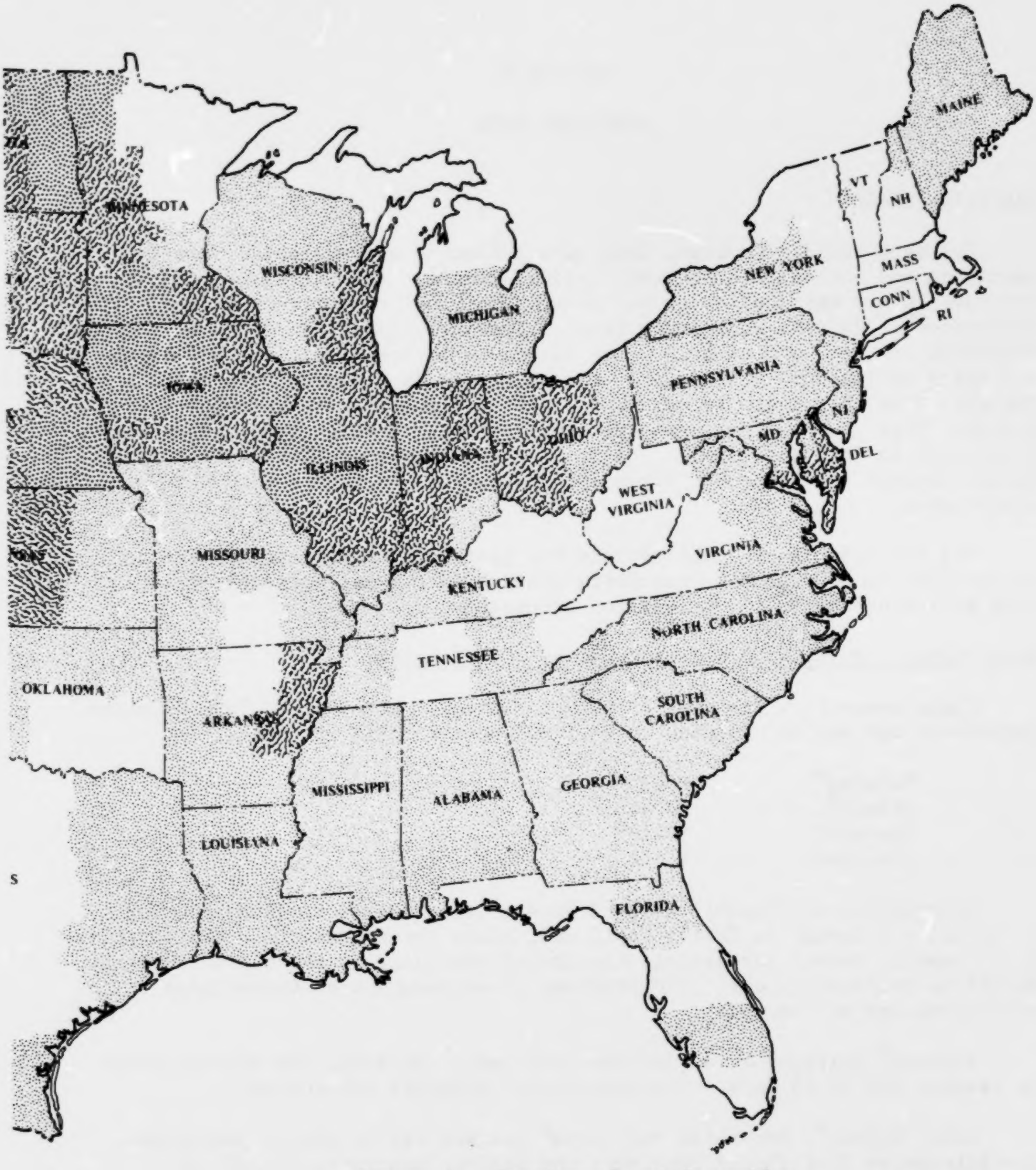

Figure 4. Density of total residue.

SECTION 6

PESTICIDE DATA

PESTICIDE USAGE

For each residue studied, data were collected and evaluated regarding pesticide and herbicide usage and residual levels. In most cases, the residual levels were quite low and are probably not significant to the environment. This is especially true of forestry waste (since little pesticide is used) and of crop waste (since tolerance levels on food crops are quite stringent). Even cattle manure pesticide residues were quite low. The main area of concern is with arsenical feed supplements in chicken manure. Most of the arsenic in the feed is passed through the chicken and is present in the manure pile. Since it is an inorganic heavy metal, it passes through the anaerobic digestion process and is returned to the environment.

The following paragraphs explain the pesticide usage data and the assumptions made regarding pesticide residue in the agricultural residue used as feedstocks in the conversion processes.

Rice (Sutter, Butte, and Colusa Counties, California)

Eight pesticides are used on rice in Sutter, Butte, and Colusa Counties, California and can be expected to be found on the hulls and straw:

Furadan®
Ordram®
Propanil
Toxaphene
MCPA
Parathion
Sevin®
2,4-D

Degradation of Propanil (1 to 3 days), Toxaphene (5 to 14 days), and 2,4-D (1 to 4 weeks) is fairly rapid and, since these pesticides are applied 2 to 3 months before harvesting, the amount remaining on the hulls and straw should be extremely small. The products of degradation of these three pesticides are not known.

Furadan® degrades at an intermediate rate. In soil, the concentration is reduced 96% in 55 days. The degradation products are unknown.

MCPA, Ordram®, Parathion and Sevin® are all fairly stable pesticides. The tolerances that should represent the maximum concentration of the pesticide on the hull or straw are:

	Tolerance (ppm)
MCPA	0.1
Ordram®	0.1
Parathion, mg/m^3	0.05
Sevin®	100

Ordram® and Parathion, both liquids at room temperature, exhibit small but significant vapor pressures at 120° to 200°C. These compounds (or in the case of Parathion, an isomer) might be distilled from the pyrolysis furnace and concentrated in the oil or water fractions. The allowed tolerances for Ordram® and Parathion are low. If all the allowable residue were to distill into the water, a maximum of 0.012 lb/hr would be present. The concentration in the condensate would be, at most, 0.8 ppm by weight.

MCPA and Sevin® have higher boiling points and would probably decompose or react to form combustion products (H_2O, CO_2). Other less desirable combustion products could also be formed. For example, the active ingredient in Sevin® is a carbamate which contains nitrogen. Midwest Research Institute, in a study on pesticide incineration,[1] found hydrogen cyanide in the offgases from incineration of nitrogen-containing pesticides. The active ingredient in Ordram® also contains nitrogen, so any decomposition of Ordram® that occurs in the converter could also result in hydrogen cyanide. If Sevin® and Ordram® were present at their tolerance levels and all of the contained nitrogen were converted to hydrogen cyanide, 1.1 lb/hr of cyanide would be present in the product gas.

Ordram® and Parathion also contain sulfur, so decomposition of these pesticides is likely to produce some volatile sulfur compounds, such as hydrogen sulfide or sulfur dioxide. The quantitites of these materials that could be produced would not be significant as air pollutants.

Other volatile decomposition products might also be formed but SRI found no information as to what these products might be.

Cotton and Barley (Kern County, California)

The physical properties of the 20 pesticides applied to cotton and barley in California are shown in Table 4. Of the 20 pesticides, 7 degrade fairly rapidly in the field and are not likely to be found in any significant amounts on the waste when it is ready to be processed. The seven are:

Toxaphene
2,4-D
Methomyl
Azodrin®
Di-Syston®
Barban
Omite®

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[1] Superscript numbers refer to documents cited in text. For a complete list of references, see the end of this report.

TABLE 4. PHYSICAL PROPERTIES OF PESTICIDES APPLIED TO COTTON AND BARLEY IN CALIFORNIA

Pesticide	Physical state	Melting point (°C)	Boiling point (°C)	Solubility	Degradation
Cacodylic acid	Solid	200	--	Alcohol, H_2O	Does not degrade on plant
Diuron (Karmex®)	Solid	158-159	Decomposes @ 180-190°C; vp[a] $148x10^{-5}$ @ 100°C	Acetone, benzene, cottonseed oil; 42 ppm in H_2O	Degrades slowly (1 year)
Nitralin (Planarum)	Solid	151-152	Decomposes vigorously @ 225°C; vp $1.8x10^{-8}$ @ 25°C	Acetone, DSMC, 2-nitro-propane, benzene; 0.6 ppm in H_2O	Degrades slowly; sensitive to UV
Paraquat	Solid (applied as solution)	Not given	Decomposes; does not melt or boil but chars; non-volatile	H_2O; insoluble in organics	Very stable; sensitive to UV
Methomyl	Solid	78-78	vp $1.6x10^{-4}$ mmHg @ 40°C	H_2O, ethanol, methanol	Appears to degrade in 7-14 days
Azodrin®	Redbrown solid	53-55	vp $7x10^{-7}$ mmHg @ 20°C	H_2O, acetone, alcohol	Degrades in 1-2 wk
Demeton	Light brown liquid	--	123-218°C @ 1 mmHg	Organic solvents; 60 ppm in H_2O	--
Phorate	Clear liquid	--	118-120°C @ 0.8 mmHg	Xylene, other organics; 50 ppm in H_2O	Tolerance 1 ppm; stable 2 yr

TABLE 4 (continued)

Pesticide	Physical state	Melting point (°C)	Boiling point (°C)	Solubility	Degradation
Kelthane®	Solid	77-78	--	Insoluble in H_2O; soluble in aromatic aliphatic solvents	Appears stable over 1 yr, but does degrade considerably
Di-Syston®	Liquid	--	62°C 0.01 mmHg	Organic solvents; 25 ppm in H_2O	Metabolizes to sulphoxide and sulphone
Omite®	Liquid	--	--	Organic solvents; insoluble in H_2O	Loses activity in about 3 wk
Treflan®	See Table 5				
Def®	See Table 5				
Sodium chlorate	See Table 5				
Toxaphene	Solid	65-95	--	--	--
Parathion	Liquid	--	157-162	--	--
MCPA	Solid	118-119	--	--	--
2-4-D	Solid	135-138	--	--	--

[a] vp = vapor pressure

Three other products -- Treflan®, Diuron (Karmex®) and Nitralin (Planquin) -- are herbicides used to kill weeds. They would not be applied directly to the weed and would probably not be present on the crop waste.

Paraquat, another herbicide, works by contact with the unwanted plant rather than attacking the seed. Paraquat could be present in small amounts on the crop waste. On heating however, Paraquat does not boil or melt but chars, so if it were present on the crop residue, it would decompose in the Pyrolysis converter.

The nine other pesticides are sprayed on the crops and degrade slowly, so they are likely to be present on the waste that is to be processed. Two of the nine, sodium chlorate and MCPA, would decompose in the converter into generally harmless products. Not enough information was obtained on the physical properties of Kelthane® to determine its end products in the converter. However, it is known to degrade considerably in one year so little is likely to be present even if it volatilizes and ends up in the condensate.

Cacodylic acid is another pesticide whose end products in the reactor are unknown. It is a stable solid having a melting point of 200°C. As an organic arsenate, it could decompose into an inorganic arsenate and end up as such primarily in the slag. The inorganic arsenates, however, have finite vapor pressures so some (perhaps 1%) might report to the condensate. Under the reducing conditions prevalent in parts of the converter, cacodylic acid might be reduced to arsine, in which case the toxic arsine would probably be found in the product gas.

The remaining five pesticides (Parathion, Methyl Parathion, Def®, Phorate, and Demeton) are all relatively stable, have finite vapor pressures below their decomposition temperatures, and are likely to report to the condensate to some extent. The Parathion and methyl Parathion isomerize on heating so the O.S. diethyl and O.S. dimethyl isomers would be the Parathion products in the condensate.

The tolerance levels for the five pesticides are as follows:

	Parts per million
Parathion	1
Methyl Parathion	0.75 (on cottonseed)
Def®	6 (on cottonseed hulls)
Phorate	0.1 (on straw)
Demeton	5 (on straw)

Since cotton waste generally does not end up on the food chain, no tolerances are set for pesticides used on cotton stalks. Tolerances are set for the concentration of the pesticides that can be present on the cottonseed and the cottonseed hulls (as shown above) but this does little to establish the concentration of the pesticide expected on the stalk. Consequently, it is almost impossible to estimate the quantity of these pesticides that might be present in the condensate.

Paraquat is the only pesticide that contains nitrogen in its structure and that is likely to be present on the waste fed to the converter. Since only small amounts of Paraquat are likely to be present on the waste, the formation of hydrogen cyanide, which is distinctly possible from the Pyrolysis processing of rice waste, does not appear a problem when the waste is composed of cotton and barley.

Rice and Cotton (Bolivar County, Mississippi)

The pesticides used on rice in Mississippi are essentially the same as those in California. Therefore, as far as the eight pesticides (below) are concerned, their end products would be the same in the Tech-Air system as in the Purox® system, except any volatile pesticide would be found in the pyrolysis oil instead of in the condenser wastewater, as in the case in the Purox® system.

The eight pesticides used on rice are:

Furadan®
MCPA
Ordram®
Parathion
Propanil
Sevin®
Toxaphene
2,4-D

The following ten pesticides are used on cotton in Mississippi:

Caparol®
Cotoran®
Def®
DSMA or MSMA
Endrin
Parathion
Sodium chlorate
Toxaphene
Treflan®
Folex®

Parathion and Toxaphene are also used on rice, so their end products in the pyrolysis system would be the same if they came from rice. (Toxaphene degrades rapidly, so it would not be present as such on cotton-waste; its degradation products are not known. Parathion is stable and could end up in the pyrolysis oil.)

Some of the physical properties of the eight other pesticides are given in Table 5. Caparol® and Cotoran® degrade fairly rapidly (30 to 90 days) and would normally be present in very minor amounts on the cottonplant at anytime, even less so at harvest.

Treflan® is an herbicide used primarily prior to the emergence of the cotton. If applied past emergence, it is laid along the side of the plant. Except for abnormal situations, Treflan®should not be found on the cotton-plant.

The remaining five pesticides are fairly stable in the field and are likely to be present on the plant when it reaches the pyrolysis furnace.

TABLE 5. PHYSICAL PROPERTIES OF PESTICIDES APPLIED TO COTTON IN MISSISSIPPI

Pesticide	Melting point (°C)	Boiling point (°C)	Solubility	Degradation
Caparol®	118-120	vp $1x10^{-6}$ mmHg @ 20°C	48 ppm in H_2O; soluble in organic solvent	Persists 1-3 mo in the field; should not be on cotton plant
Cotoran®	163-164.5	--	80 ppm in H_2O; soluble in ethonol, aceton, and isopropanol	Half-life: 60-75 days
Def®	Liquid at room temperature	vp 0.3 mmHg @ 150°C	Insoluble in H_2O, soluble in organic solvents	Stable to heat and acids
DSMA/MSMA	132-139	--	36% soluble in H_2O	Slowly decomposes at elevated temperatures. Could form methyl arsine under reducing conditions.
Endrin	200	vp $2x10^{-7}$ mmHg @ 25°C	Generally insoluble	Rearranges when heated over 200°C
Folex®	Liquid at room temperature	--	--	Oxidizes readily to DEF
Sodium chlorate	248	Decomposes	Soluble in H_2O and alcohols	Decomposes on heating
Treflan®	48-49	vp 0.18 mmHg @ 96-97°C	Insoluble in H_2O; soluble in acetone ethanol, and xylene	85-90% is lost in 6-12 mos in the field

Three of the five, sodium chlorate, Endrin, and DSMA/MSMA, either rearrange or decompose on heating. The product of rearrangement of Endrin is not known but is presumably less toxic. Sodium chlorate decomposes to sodium chloride and oxygen, so no problems are anticipated from this material. DSMA/MSMA, however, forms a highly toxic methyl arsine at elevated temperatures under reducing conditions. With a low solubility in water and a boiling point of 2°C, any methyl arsine formed is likely to end up in the pipeline gas product.

Def® and Folex® (the remaining pesticides), are defoliants normally applied on the cottonplant when it is fully grown. Def® is a stable compound; Folex® oxidizes readily to form Def® so it could be present in measurable amounts in the pyrolysis oil, if any oil is produced.

PESTICIDES AND HERBICIDES USED ON SUGARCANE IN FLORIDA

Both pesticides and herbicides are used in sugarcane plantations. Preemergence and postemergence herbicides are both used, but they are directed onto the weeds and soil, and away from the cane stalks. The two sources of herbicides in collected cane and cane trash are the overspray that may fall onto the plant and the soil that may be included in the collection process. While insecticides are directed onto the plant itself, residues are minimized by proper timing of the application. Generally, no sprays are applied within 30 days of harvest. Residues are quite low and carefully controlled, since some of the bagasse is used as dairy cattlefeed and the tolerance levels are quite low.

Sugarcane Insect Pests

The following insects cause damage to sugarcane:

Sugarcane borer
Wireworms
Fall armyworm
Climbing cutworm
Glassworm
Yellow sugarcane aphid
West Indian sugarcane delphacid
Sharp-nozed grain leafhopper
Spittlebug
Gray sugarcane mealybug
Lesser cornstalk borer
White grubs
Leafroller

Pesticides

The pesticides presently used in Florida sugarcane fields are listed in Table 6.

TABLE 6. SUGARCANE PESTICIDES

Trade name	Chemical name and manufacturer	Application rate
Azodrin®	Dimethyl phosphate of 3-hydroxy-N-methyl-cis-cortonamide (Shell Chemical Company)	3 to 4 lb/acre
Diazinon	O,o-diethyl o-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate (Ciba-Geigy Corporation)	2 to 4 lb/acre
Parathion	O,o-diethyl o-p-nitrophenyl phosphorothioate (Monsanto and Stauffer)	2 to 4 lb/acre
Furadan®	2,3-dihydro-2,2-dimethyl-7-benzofuranyl methyl carbamate (FMC Corporation)	2 to 4 lb/acre

Residue Concentration

Assuming four applications of each of the above pesticides at the highest level indicated, a maximum of 64 lb (4 x 4 x 4) would be applied per acre. Since about 100 tons of cane plant are produced per acre, the concentration would be <0.03% wt of pesticide residue. If we consider only the pesticide that touches the plant (i.e., overspray), the maximum concentration is less than 0.02% wt. Also, since one-third to one-half of the pesticides are applied to the plantings and immature stalks, and no pesticides are applied within 30 days of harvest, concentrations at harvest are probably much less than 100 ppm. Estimated actual pesticide residues in the collected cane and leafy trash are 1 to 10 ppm.

Herbicides for Weed Control

The main herbicides utilized in cane fields are AAtrex®[*] (atrazine) and dalapon.[†] Both compounds damage plants and care is taken to direct sprays away from the sugarcane plants. Maximum application for preemergence or postemergence control is 24 lb/acre/yr.

Some soil is picked up with the cane and trash; therefore, an estimate of the herbicide concentration in the collected trash is needed. We assume that about 5% soil is collected in the harvest, that no washing or cleaning of the cane occurs, and that any herbicides picked up remain with the cane trash (i.e., the worst case). In fact, the dirt would probably be removed by either a wet or dry screening before combustion.

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[*] Aatrex® = Atrazine, 2-chloro-4-ethylamino-6-isopropylamino-S-triazine (Ciba-Geigy).

[†] Dalapon = Sodium salt of 2,2-dichloropropionic acid (several producers).

Herbicide Soil Concentration

Assuming 24 lb of herbicide is applied per acre (44,000 ft^2) and no degradation or runoff, the concentration is about 5.45×10^{-4} lb/ft^2. If we assume a uniform distribution of the herbicide in the top 6 inches of soil, then the concentration is 1.09×10^{-3} lb/ft^3. Since the soil is a wet, heavy muck, its density is over 100 lb/ft^3. Therefore, the final herbicide concentration in the soil is 1.09×10^{-5} lb/lb soil or around 11 ppm. Since only 5% soil is collected with the can trash, the maximum herbicide concentration (assuming no degradation or runoff) in the cane trash is less than 0.5 ppm.

PESTICIDES USED ON CATTLE MANURE IN COLORADO

Cattle manure may contain pesticide residues from three sources: feed-through fly control, flyspray control, and pesticide residue in the feed. In this analysis, we assume the worst case (i.e., the maximum concentration of pesticide residue in the manure). The hypothetical feedlot is assumed to use both a feed-through and a mist spray to control flies. Residue from the cattle feed is assumed negligible.

Sprays and Baits

Several pesticides (Table 7) can be used in spray or bait programs for fly control. The sprays are generally directed onto the manure and are

TABLE 7. PESTICIDES USED FOR FLY CONTROL IN CATTLE FEEDLOTS

Pesticide	Level (%)	Application method
Rabon®, Ronnel	-	Feed-through
Dichlorvos	1	Mist spray
Dibrom®	1	Mist spray
Baytex®	1	Residual spray
Cygon®	1	Residual spray
Rabon®	1 to 2	Residual spray
Ravap®	1 to 2	Residual spray
Methoxychlor	-	Residual spray
Ronnel	-	Residual spray
Malathion	-	Residual spray
Trichlorfon (Dipterex®)	-	Residual spray
Diazinon	-	Residual spray
Ciodrin®	-	Residual spray
Dichlorvos	100 lb/5 miles of bunker	Bait

used 1 to 2 times per week during the fly season (about 4 months' duration). Mist sprays are used for area-wide control, residual sprays are applied to specific areas or directly onto the cattle.

Baits also may be used for fly control. Generally, the baits are spread near the feeding troughs, and not broadcast over the manure. Very little bait would probably be collected with the manure.

This analysis uses a mist spray program, utilizing both Dichlorvos and Dibrom®.

Feed-Through

During the fly season, a feed-through may be used. This analysis considers Rabon® to be fed. The residual Rabon® is excreted and would be collected with the manure.

Discussion

During the maximum application period, when both sprays and feed-throughs are used, the maximum concentration of pesticides in the manure is less than 100 ppm as shown below:

	Concentration (ppm)
Sprays	
Dibrom®	33
Dichlorvos	51
Feed-through	
Rabon®	10
Total	94

This value (94 ppm) is the maximum that could be expected directly after a combined spray and feed-through application. Since the pesticides used are organophosphates and the concentration in the manure is low, no detrimental effect is anticipated on the anaerobic bacteria or the process equipment.

The analysis assumes that a fresh manure collection system is installed and that no fly control program would be used, since the source of the pesticide residues would be removed.

Also, assuming 5-month collection cycles, there are some periods with no pesticide applications; thus, only a small percentage of the manure would contain the high concentrations calculated here.

On a 5-month collection cycle, nearly all of the old pesticide residue (those over 30 days old) have degraded. Thus, a realistic concentration for a 5-month collection cycle is the concentration produced during the last 30 days only. This would be about 20% of the maximum levels calculated in Table 8, or 20 ppm or less.

TABLE 8. MIST SPRAY CALCULATION

Basis

2 applications per week
4-month fly season
32 total applications

Materials

Dichlorvos (Vapona®, DDVP):
6.25 oz, 44.5% Vapona® in 5 gal diluted spray per acre

Dibrom® (Naled®):
3 oz, 60% Dibrom® in 5 gal water spray per acre

Calculations

Active ingredients

Dichlorvos:	2.78 oz active ingredient/acre per application
Dibrom®:	1.8 oz active ingredient/acre per application
Total Dichlorvos:	32 applications x 2.78 oz = 89 oz or 5.5 lb active ingredient/acre
Total Dibrom®:	32 applications x 1.8 oz = 57.6 oz or 3.6 lb active ingredient/acre

There are two types of feedlots, surfaced and unsurfaced. On surfaced feedlots, generally 150 sq ft is required per animal. On unsurfaced feedlots, 400 sq ft per animal is required. An unsurfaced feedlot is assumed as this results in a higher concentration of pesticide residue.

Defecation rate = 5.5 lb dry matter per head per day; at 110 head per acre, 605 lb/acre-day

Assuming the maximum possible concentration:

Dichlorvos	5.5 lb active ingredient/acre
Manure	108,900 lb dry matter/acre per 120 days
Concentration	0.0051% wt or 51 ppm
Dibrom®	3.6 lb active ingredient/acre
Manure	108,900 lb/acre per 120 days
Concentration	0.0033% wt or 33 ppm

PESTICIDES AND HERBICIDES USED ON WHEAT IN COLORADO

The wheat residue considered for anaerobic digestion is unlikely to contain significant pesticide or herbicide levels. As the data in Table 9 show (except for the herbicide 2,4-D) only a small percentage of the acreage is treated with pesticides or herbicides. The seed treatment insecticides and fungicides are essentially lost to the soil and are not collected in the wheat harvest. The other herbicides listed are applied at least 30 days before harvest and do not appear on the harvested product above the tolerance levels for human consumption. Therefore, the analysis considers the cattle manure anaerobic digestion case with wheat residue added to contain less pesticide/herbicide residue than the straight manure digestion.

TABLE 9. PESTICIDES AND HERBICIDES APPLIED TO WHEAT IN COLORADO

Material	Planted acreage treated (%)	Active ingredient	Rate/ acre	Time of Application
Herbicides				
2,4-D	20.7	2,4-Dichlorophenoxyacetic acid	2. lb	May-June
Bromoxynil	6.5	3,5-Dibromo-4-hydroxybenzonitrile	0.5 lb	May-June
Barban	2.4	4-Chloro-2-butynyl-m-chlorocarbanilate	0.75 lb	May-June
Insecticides				
Endrin	1.4	Hexachloroepoxyoctahydro-endo, endo-dimethanonaphthalene	0.5 lb	July
Parathion	1.0	O,O-Diethyl-O-P-nitrophenyl phosphorothioate	0.5 lb	
Seed treatments (insecticides)				
Heptachlor	4.3	Heptachlorotetrahydro-4-7 methanoindene	1 oz	April
Lindane	3.2	Benzene hexachloride	0.5 oz	April
Fungicides (limited to see treatments)				
PMA	17.6	Phenyl mercuric acetate	1 oz	April
Captan	10.0	N-(Trichloromethylthio)-4-cyclohexene 1,2-dicarboximide	5 oz	April
Terracoat® L-205	7.5	5-Ethoxy-3-trichloromethyl-1, 2,4-thiodiazole	0.4 lb	April

PESTICIDE AND HEAVY METAL RESIDUE IN CHICKEN MANURE IN ARKANSAS

Since detailed data are not avilable for Washington County, Arkansas, a worst case is assumed, which includes arsinicals for therapeutic purposes and growth promotion, a complete fly control program, and a chemical pesticide control program for infestation of lice and mites. The data derived are the theoretical upper limit of possible concentrations of the specified compounds that might be found in the manure.

Feed Additives

Two principal compounds used are arsanilic acid and 3-nitro-4-hydroxyphenylarsanic acid. These arsinicals are generally excreted unchanged in chemical structure and with no evidence of conversion to inorganic forms of arsenic. The maximum feed levels and concentrations in manure are shown below:

Compound	Maximum concentration in feed (ppm)	Maximum concentration in manure[a] (ppm)
Arsanilic acid	100	87
3-nitro-4-hydroxyphenyl-arsanic acid	50	44

[a] Based on 87% of the feed arsaenic excreted with the manure

Fly Control Programs

Some products used for fly control in the manure in poultry houses are: Baytex®, Co-Ral®,* Cygon®,* Diazinona®,* Dibrom®, Ronnel,* Malathion, Pyrethrins, Rabon®, Sevin®, and DDVP. The type of spray and ratio for widely recommended products are listed in Table 10.

In large operations where manure collection is most feasible, the manure is removed from the houses at least every other day and stockpiled. Therefore, a major source of pesticide residues in poultry manure would come from the treatment of stockpiles. As manure dries, it becomes less of a breeding site for flies.

As a sample calculation, we make the following assumptions:

- Manure density = 60 lb/ft^3
- Manure production = 0.0062 ft^3/bird/day

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*Can be sprayed under cages only.

TABLE 10. FLY SPRAYS AND APPLICATION RATES

Material	Rate	Restrictions
Residual Spray		
Cygon® 4E Ronnel 24% EC	8 oz/1500 ft^2	Do not apply to birds or with birds in house
Space Spray		
DDVP 0.5% Dibrom® 37% EC Ronnel 24% EC	Not applicable	
Larvicides		
Cygon® 4E	8 oz/1000 ft^2 of droppings	Do not spray directly on poultry or feed
Rabon® 24% EC	26 oz/500 ft^2 of droppings	

- Cygon® 4E at 8 oz/1000 ft^2 of manure = 0.5 pt = 0.25 lb of active ingredient

- Assumed pile depth = 1 ft

The above calculations yield 25 lb of active ingredient per 60,000 lb of manure.

Even if there were four applications to the manure before it dried, and the pesticide did not degrade, the concentration would be negligible. The same should be true for the other materials. The conclusion is that the pesticide residue from fly control in poultry manure is negligible (less than 5 ppm).

Ectoparasite Control

Among the mites that attack poultry are chicken mite, northern foul mite, scaly-leg mite, depluming mite, and tropical fowl mite. Of the lice that attack poultry, the body louse is the most common.

The recommended treatment is to dust the birds. As an example, 1 lb of 5% Sevin® dust will treat 100 birds. This amounts to 0.0005 lb of active ingredient per bird. Applications are not made more often than every 4 weeks. Assuming a growing period of 9 weeks for a broiler, the broiler would not receive more than two applications. For a layer, who is productive for approximately 18 to 24 months, she could get perhaps four treatments per year in a 12-week period.

In the worst case, the maximum concentration in the manure would be:

Wet manure per bird/day = 0.25 lb

12 weeks = 84 days

Total manure = 21 lb

4 applications @ 0.0005 = 0.002 lb

Assume 20% falls off bird onto manure = 0.0004 lb

0.004 lb active ingredient/21 lb manure = 0.0019% (19 ppm) concentration

Thus, pesticide residues in manure due to ectoparasite chemical control are negligible.

Based on 430,000 tons/yr of chicken manure, the total quantity of arsenic compounds used per year could be as high as 86,000 lb/yr.

Total pesticide residue from fly, lice, and mite control amounts to less than 25 ppm. This figure should be much lower, allowing for normal degradation of these pesticides.

PESTICIDES USED IN FORESTRY APPLICATIONS IN THE UNITED STATED

Based on the forest pests involved and the amount of material used, insecticide residue in forest residue for Humboldt County, California and Green County, Alabama would be negligible. As a national average, less than 1% of all forest acreage receives any insecticide treatment. In addition, the two counties involved are not considered regions where insect damage has had a high economic impact.

Zectran®, made by Dow Chemical Co., is the major insecticide used in forests. It is effective against the Spruce budworm, Douglas Fir Tussock moth, and gypsy moth, which are the three major species of forest insects that are treated in the U.S. Zectran® has effectively replaced DDT, which is no longer used, except under emergency permits; it is endorsed by the U.S. Forest Service. The majority of the material is used in the Northwest.

No significant quantities of herbicides or fungicides are used in the forests nor would be found in the forest residue. Table 11 shows the materials used.

TABLE 11. FOREST AREA AERIALLY SPRAYED WITH INSECTICIDES IN THE U.S.[a]

Material	Acres treated (000)	Active ingredient	Rate/acre (lb)
DDT	425	Dichlorodiphenyltrichloroethane	1
Carbaryl (Sevin®)	90	1-Naphthyl methylcarbamate	1.0
Zectran®	470	4-(Dimethylamino-3,5-xylyl) methylcarbamate	0.15
Trichlorofon (Dylox®)	77	Dimethyl (2,2,2-trichloro)-1-hydroxyethyl phosphonate	1.0
B.T. (Dipel®)	15	Live spores of Bacillus Thuringiensis-Berliner	1 to 2

[a] Source: Reference 2.

PESTICIDES AND HERBICIDES USED ON FIELD CROPS

Corn (Missouri and Iowa)

Herbicides used on corn in Missouri and Iowa are listed below, along with EPA residue tolerances:

Herbicide	Tolerance (ppm)
Lasso®	0.02
AAtrex®	15
Atrazine	15
Lasso® II	0.02
2,4-D	20
Bladex®	0.05

Most of these herbicides are applied as preemergent materials; the residual material at harvest is very low.

Insecticides used in both areas are Furadan and Counter; in Missouri, Dyfonate®, Thimet®, and Dasanit® are also used. Tolerance levels are as follows:

Insecticide	Tolerance (ppm)
Counter® (Terbufos)	0.5
Dyfonate®	N/A
Dasinit®	1
Furadan® (Carbofuran®)	25
Thimet®	0.5

Degradation rates appear relatively rapid for this group of insecticides judging from the tolerance levels. Furadan® degrades from 25.4 to less than 1 microgram/cm^2 in 55 days.

Sunflowers (North Dakota)

The only pesticides used on sunflowers in Traill, North Dakota are the insecticides Endosulfan and methyl-Parathion. The residue tolerances as set by EPA are 2 ppm on sunflower seeds for Endosulfan, and only 0.2 ppm of methyl-Parathion. Neither material poses a problem at these levels.

Barley and Wheat (North Dakota)

Pesticides used on barley and wheat in North Dakota are listed below, with residue tolerances as given by EPA:

	Tolerance (ppm)
Herbicides	
2,4-D	20
MCPA	2
Barban	0.1
Insecticides	
Malathion	135
Parathion	1

Wheat (Missouri)

The pesticides used on wheat in Marshall, Missouri include the herbicides 2,4-D and MCPA and the same seed treatments as for barley in Traill, North Dakota. Toxaphene is the principal insecticide used. The residue tolerance set by EPA is 5 ppm; the degradation rate is very rapid. The effectiveness of the insecticide lasts only 5 to 14 days in the air.

SECTION 7

COLLECTION AND TRANSPORTATION

FORESTRY RESIDUE

Collection

As in the case of most agricultural residue, the cost of collecting logging residue is a major impediment to implementation. Conventional logging practice involves felling the trees, trimming off the branches and tops, and loading the trunks onto trucks for transportation to the lumber or pulp mill. The branches and tops are removed because their bulk prevents safe stacking of the logs on the trucks. Too, the branches would stick out beyond the sides of the trucks, making highway transport impossible. Also, handling the whole tree with branches is considerably more difficult than handling the trunk alone.

Collection of the remaining "slash" has to date been uneconomical. Because of the variable nature of the material and its random distribution, collection is manually performed, although items such as stumps might be mechanically removed. (Several stump-pulling machines are under development.)

Manual collection involves two options for transporting the residue to the power plant: the residue is collected in bins and shipped directly to the power plant; or more likely, a chipper is used to reduce the volume and prepare the material for direct feeding to the boiler. A major problem is the inclusion of dirt in the product.

Some items that are presently not logged, such as dead or diseased trees or undesirable trees (wrong varieties, saplings, crooked or deformed trees), could be cut and added to the pile.

Land Disruption from Collection

Very little land disruption is anticipated in collecting logging residue. Since active logging is in progress at the site of residue collection, common facilities (roads, etc.) can be shared. Less than 1 acre would be required for the collection, field storage, chipping, and chip storage at a logging site.

Air Emissions

There are four main sources of air emissions in the collecting and using of logging residue:

- Equipment used in the field for collecting and chipping
- Equipment used to transport chipped residue
- Equipment used during loading and unloading of chips
- Equipment used during combustion, plus the combustion process itself

Collecting and Chipping Equipment--

If portable chippers are used, the chipper is brought into the area of recently felled trees, and the slash is fed into the chipper. Chippers can process about 600 to 700 lb wood/hp/day. A 3000-ton/day operation (6,000,000 lb divided by 600 lb/hp), requires about 10,000 hp/day. If diesel engines are used as power supplies for the chippers, about 1 gal of diesel fuel is consumed per 20 hp/hr. In a 24 hr day, 417 hp/hr are required, consuming about 20.8 gal of diesel fuel. The chipper engines produce approximately 21 lb/hr of hydrocarbons, plus NO_x emission, and 42 lb/hr of CO emission.[3]

Loaders are not required since the chipper discharges directly into the truck bed. Dust emissions are a concern, but could vary depending on the precaution taken.

Transportation Equipment--

If the maximum one-way hauling distance is 50 miles and the average is 25 miles, the 3000-ton/day operation would use 75,000 ton-miles of transportation per day. The hauling would be performed by large diesel truck/trailer combinations. If a vehicle carries 40 tons per trip, 75 round trips (3750 miles) would be driven per day. The emission factors used[4] are 28.7 g/mile CO, 20.9 g/mile NO_x, 1.3 g/mile particulates, 2.8 g/mile SO_2, and 4.6 g/mile hydrocarbons. Thus, the total emission from transportation equipment is:

NO_x	172 lb/day	or	7 lb/hr
CO	237 lb/day	or	10 lb/hr
HC	37 lb/day	or	1.5 lb/hr
SO_2	23 lb/day	or	1.0 lb/hr
Particulates	10.7 lb/day	or	0.4 lb/hr

Equipment Used to Load and Unload Chips--

Large trucks would haul the chips to a storage area and unload them, probably on a portable tilting platform with the chips discharging from the rear of the truck. Minimum handling of the chips is needed once the dump is completed. Actual emission from the dumping and handling equipment varies widely, depending on the particle size, moisture content, and weather conditions. If the chips are both damp and relatively large (a minimum of 1/2 inch x 1/2 inch), no serious particulate emissions are expected from the handling equipment.

SUGARCANE TRASH

Harvesting

The use of leafy sugarcane trash as an energy source requires imporved harvesting. To date, the economic benefit of using the trash as fuel has been more than offset by the cost of harvesting. Harvesting techniques vary from plantation to plantation, but are generally classified as manual or mechanical. In Florida, 75% of the cane is harvested manually; the remaining 25% is harvested mechanically.

If the present high cost can be overcome and trash harvesting becomes economically attractive, the trash and cane must be separated. In manual harvesting, the trash and cane would probably be separated in the field as the cane is cut. The cane would be hauled to the mill for sugar extraction, while the trash would go directly to the boiler. Manual harvesting should present less difficulties with dirt and rock inclusion than mechanical harvesting.

In mechanical harvesting, the trash can be separated from the cane at the field or at the mill. If a field-cleaning technique is used, the harvester would pick and cut up the entire stalk and separate the trash, probably by air-classification. If field cleaning is not used, the entire stalk would be transported to the mill, where a wet cleaning system would be used. The wet trash would be dried before feeding into the boiler. Both techniques are presently used in Hawaii.

A discussion of harvesting and separation techniques in Hawaii appears in the literature.[5] However, harvesting cost is the main roadblock to the use of leafy trash and further study of the subject is needed. Basically, the major problems with harvesting the trash are:

- Cost
- Soil inclusion
- Separation of cane and trash
- Sugar yield loss due to inclusion of trash in the milling operation
- Mechanical harvesting techniques need to be perfected
- Florida cane crop and soil characteristics are different than in the Hawaiian fields and different equipment is needed

Transportation and Storage

Sugarcane trash and leaves are transported in the same way as sugarcane is presently handled. The cane is loaded into wagons with a 4-ton capacity. Four wagons are connected and pulled out of the field with 4-wheel-drive tractors. At the roadside, the cane is dumped into trailers for highway transport or into railcars for rail transport to the mill. Highway trailers carry 20 tons per load.

If the average distance to a central plant is 25 miles (50 miles roundtrip) and the trash collected is 1,000,000 tons/yr, then 50,000 roundtrips (2,500,000 miles) are driven per year. The estimated emissions from equipment used to transport cane trash are given in Table 12.

TABLE 12. ESTIMATED EMISSIONS FROM EQUIPMENT USED TO TRANSPORT CANE TRASH

	g/mile[a]	x Miles	= Total g/yr	= lb/yr	lb/10^6 Btu
Particulate	1.3	2.5×10^6	3.25×10^6	7,159	0.001
Sulfur oxide	2.8	2.5×10^6	7×10^6	15,419	0.002
Carbon monoxide	28.7	2.5×10^6	71.75×10^6	158,040	0.03
Hydrocarbon	4.6	2.5×10^6	11.5×10^6	25,330	0.004
Nitrogen oxide	20.9	2.5×10^6	52.25×10^6	115,089	0.02

[a] Source: Reference 3

The emissions per unit energy (lb/10^6 Btu) assume 1×10^6 ton/yr of cane trash containing 50% moisture is burned to produce steam at a conservative net heat output of 3000 Btu/lb wet trash. Thus, the heat output of 6×10^{12} Btu/yr is assumed from 1×10^6 tons/yr of cane trash.

TRANSPORTATION OF CROP RESIDUE TO POWER PLANTS

In all cases considered for use of crop residue, the following parameters for transportation are used:

Distance: 25 miles (average, one way)
Vehicle: 20-ton capacity diesel truck trailer
Emission factors: from US EPA AP-42, "Compilation of Air Pollution Emission Factors," Supplement 5, page 3.1.5-2, Table 3.1.5-1.

Table 13 shows the emissions from transportation equipment used to ship residue from three sites: Traill, North Dakota; Marshall, Missouri; and Sibley, Iowa.

MANURE

Since manure generation occurs at large confined feedlots, it is logical to construct on-site anaerobic digestion facilities. Thus, no net increase in collection costs, transportation costs, or emission levels would be noted over the present system.

Details of transportation to, and feeding into, the digesters would vary from location to location. In the cases presented here, the assumption is that the pen-cleaning operation stacks the manure adjacent to the digester where conveyors feed the digester. This operation is described in greater detail in the following section.

TABLE 13. EMISSION FROM EQUIPMENT USED TO TRANSPORT RESIDUE

	Transported Tons/yr	Energy Content, Dry (Btu/lb)	Moisture (%)	Energy Content, Wet (Btu/lb)	Net Total Energy (Btu/yr)
Traill, N. Dakota	76,000	7,980	28	5,746	8.73×10^{11}
Marshall, Missouri	43,500	7,980	40	4,788	4.16×10^{11}
Sibley, Iowa	7,500	8,100	50	4,050	6×10^{10}

Transportation Emissions

		g/mi	mi/yr	g/yr	lb/yr	$lb/10^6$ Btu
Traill, N. Dakota	Particulates	1.3	190,000	247×10^3	544	0.0006
	SO_2	2.8	190,000	532×10^3	1,172	0.0013
	CO	28.7	190,000	5453×10^3	12,000	0.014
	Hydrocarbons	4.6	190,000	874×10^3	1,925	0.002
Marshall, Missouri	Particulates	1.3	108,750	141×10^3	312	0.0007
	SO_2	2.8	108,750	304.5×10^3	671	0.0016
	CO	28.7	108,750	3121×10^3	6,874	0.0165
	Hydrocarbons	4.6	108,750	500×10^3	1,101	0.0026
	NO_x	20.9	108,750	2273×10^3	5,006	0.0120
Sibley, Iowa	Particulates	1.3	18,750	24,375	54	0.0009
	SO_2	2.8	18,750	52,500	116	0.0019
	CO	28.7	18,750	538,125	1,185	0.020
	Hydrocarbons	4.6	18,750	86,250	190	0.003
	NO_x	20.9	18,750	391,875	863	0.014

SECTION 8

ANAEROBIC DIGESTION

LOCATIONS

This section considers three cases for the application of anaerobic digestion to the production of methane gas from agricultural residue. The following residues and sites, selected from the National Waste Inventory, offer the best potential for commercial application because of the large quantities of wastes available and the applicability of anaerobic digestion to the processing of those wastes.

The first case involves anaerobic digestion of cattle manure in Weld County, Colorado, where approximately 400,000 tons of feedlot cattle manure are generated each year. The second case, also in Weld County, considers the use of approximately 200,000 tons of wheat residue per year as a supplement to the cattle manure. The third case selected is Washington County, Arkansas, where 430,000 tons of chicken manure are available per year.

PROCESS DESCRIPTION

The degradation of waste by anaerobic digestion requires a variety of anaerobic and facultative bacteria. Complex materials such as cellulose and protein are first hydrolyzed by extracellular enzymes. The smaller organic molecules are then fermented by acid-forming bacteria to produce simple organic acids such as acetic, propionic, and butyric acids. These acids are then fermented by bacteria to produce methane and carbon dioxide. Figure 5 illustrates the fermentation of complex wastes.

The quantities of waste material to be fed to the anaerobic bacteria are listed in Table 14. Characteristics of the materials with respect to contaminants such as pesticides are described in section 6.

Different collection cycles were chosen for cattle manure to show the effect of natural manure digestion on the system gas yield. The solids content of manure varied from 20% solids for fresh manure with urine to an average of 50% solids for manure collected every 6 months.

Completely mixed digesters with no solids recycle (Figure 6) are considered for fermentation of agricultural waste. The slurry feed is prepared by mixing water with the waste solids, producing a solids concentration of 7% for chicken manure, 10% for cattle manure, and 10% for cattle manure and wheat residue. (Input water, if required, is pumped

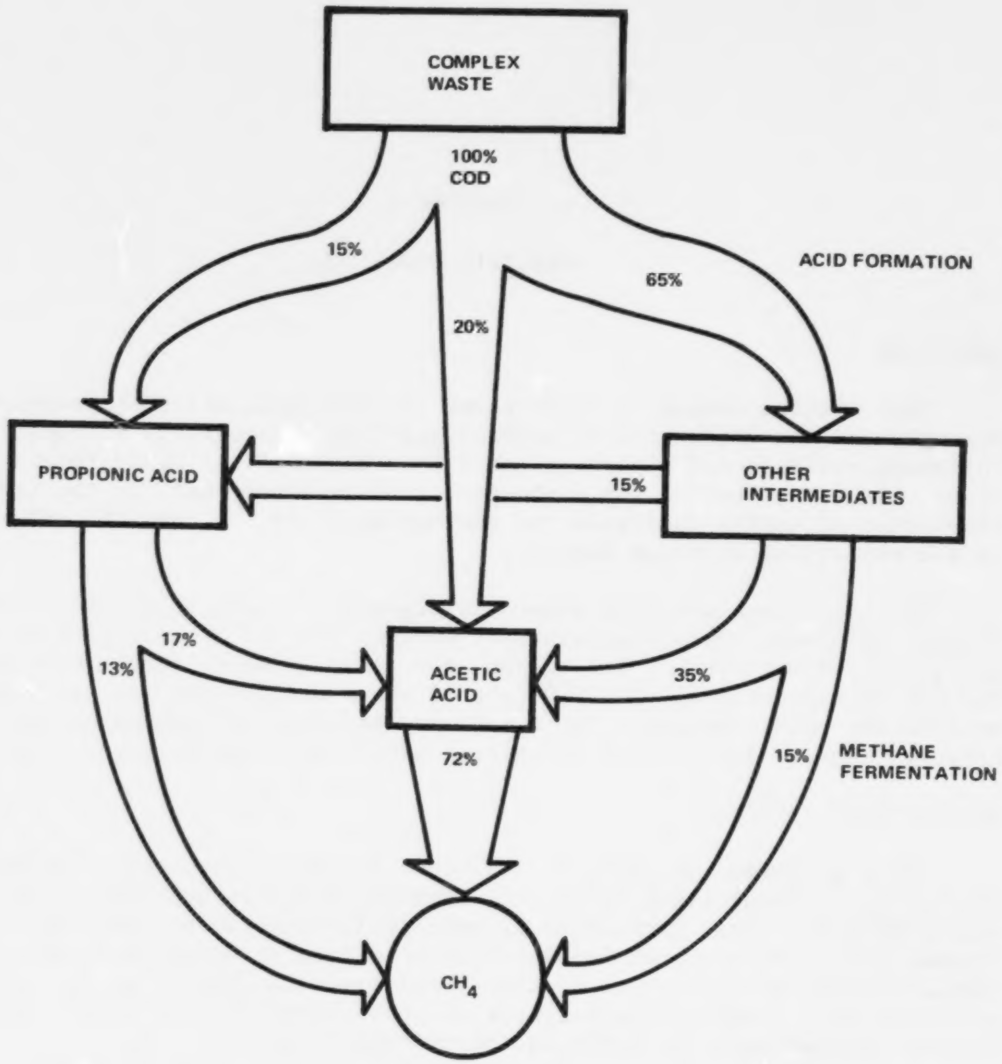

Figure 5. Pathways for the methane fermentation of complex wastes (source: reference 6).

from wells at 50°F.) Greater dilution of the chicken manure is necessary because of the higher nitrogen content and the possible inhibitory effect of ammonia on the process. The chicken manure with liquid recycling requires continual removal of ammonia from the recycled liquid and the anaerobic bacteria. The following discussion shows that liquid recycling may be very important in terms of energy conservation.* Liquid recycling also conserves water and reduces water pollution.

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*Because of evaporative cooling in the dewatering process, the temperature of the recycled water has been assumed to be approximately 75°F (as opposed to 50°F for makeup water).

TABLE 14. QUANTITIES OF WASTE MATERIAL USED IN ANAEROBIC DIGESTION

Case	Location		10^6 lb/day (Dry basis)
1A	Weld County, Colorado	Cattle manure (fresh)	2.20
1B	Weld County, Colorado	Cattle manure (5-month collection cycle)	1.41
2	Weld County, Colorado	Cattle manure (fresh) and wheat residue	2.2 + 1.1
3A	Washington County, Arkansas	Chicken manure (without liquid recycle)	3.08
3B	Washington County, Arkansas	Chicken manure (with liquid recycle	3.08

For this analysis, aboveground digesters were assumed in making heat loss calculations. In commercial installations, in-ground vessels may be installed for economic reasons.

The digestion tanks are assumed to be 110 ft in diameter and 35 to 40 ft deep. A sample plot plan (Figure 7) shows 32 digesters. The actual number of digesters for the cases considered varies from 19 to 33. A retention time of 20 days has been assumed for all cases. (An economic optimization study might lead to a design with a lower retention time.) The digesters are mixed by recirculating the product gas and heated by direct firing of the product gas (625 Btu/scf or 65 volume % CH_4) in boilers. Heat losses are calculated assuming that the digester operating temperature is maintained at 95°F with an average yearly ambient temperature of 50°F. The tanks are insulated with 2 inches of foam insulation.

After gravity settling, the digested sludge solids are further dewatered by vacuum filtration to produce a cake with 25% solids content.

The gross and net energy production figures are summarized in Figure 8.[*] Because of the relatively low gas yield for case 3A, it is excluded from most comparisons. Simplified material balances are shown on Figure 9. (See Appendix A for more details on the process and more complete mass and energy balances.)

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[*] Note that the high input slurry heating requirements could possibly be partially met by use of solar heaters but at a relatively high capital investment cost.

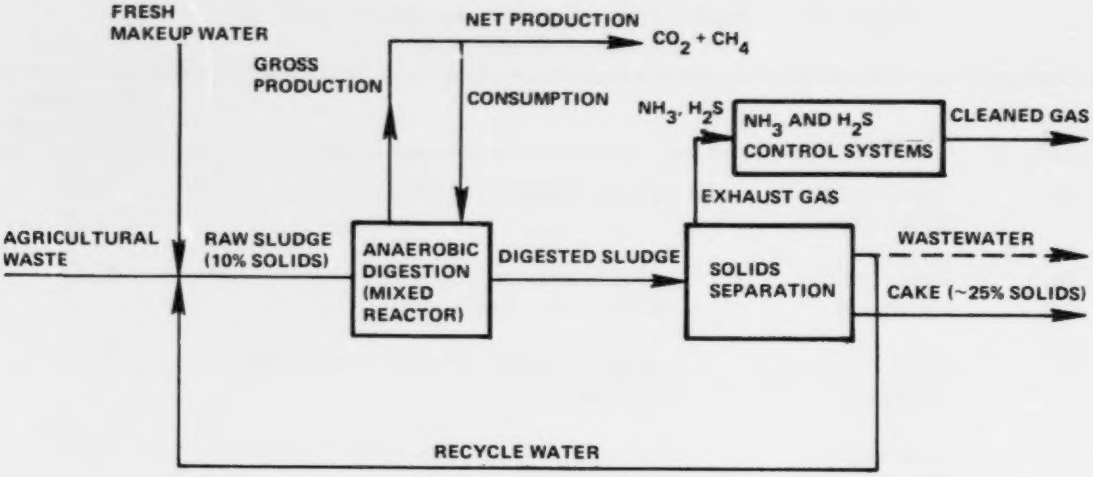


Figure 6. Anaerobic process for manure digestion.

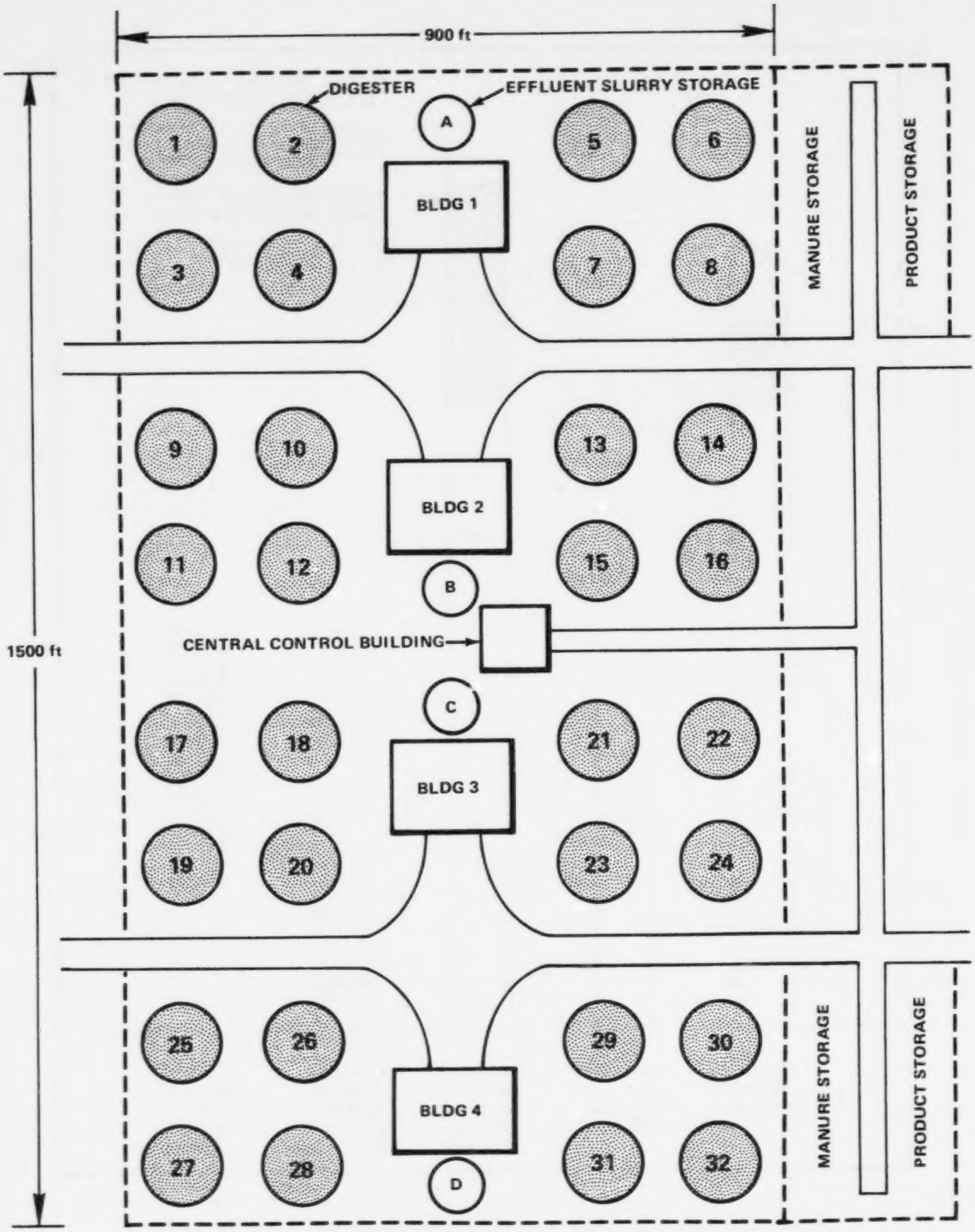
The potential air emission sources from the digestion operation include the following:

1. Boilers for digester heating (SO_2, NO_x)
2. Heavy equipment for hauling manure and product (SO_2,NO_x)
3. Tank leakage (H_2S, NH_3)
4. Thickener (H_2S, NH_3)
5. Vacuum pump exhaust (H_2S, NH_3)
6. Manure storage piles (H_2S, NH_3)
7. Product storage (H_2S, NH_3)

In our analysis, source 2 is considered negligible; sources 3, 6, and 7 are not any higher than current losses from decomposition of manure in the feedlots and have not been quantified; the thickener is covered to control source 4, with offgases vented through the H_2S and NH_3 control system for source 5. Source 1 is the only source quantified for the comparison of anaerobic digestion with other gas-producing options.

The potential water emission sources include:

1. Manure storage area runoff water
2. Product area runoff water
3. Any water not recycled



NOTE: OPERATING BUILDINGS 1 TO 4 CONTAIN SLURRY PREPARATION EQUIPMENT, BOILERS FOR DIGESTER HEATING, AND SLURRY DEWATERING EQUIPMENT.

Figure 7. Sample plot plan showing 32 digesting tanks.

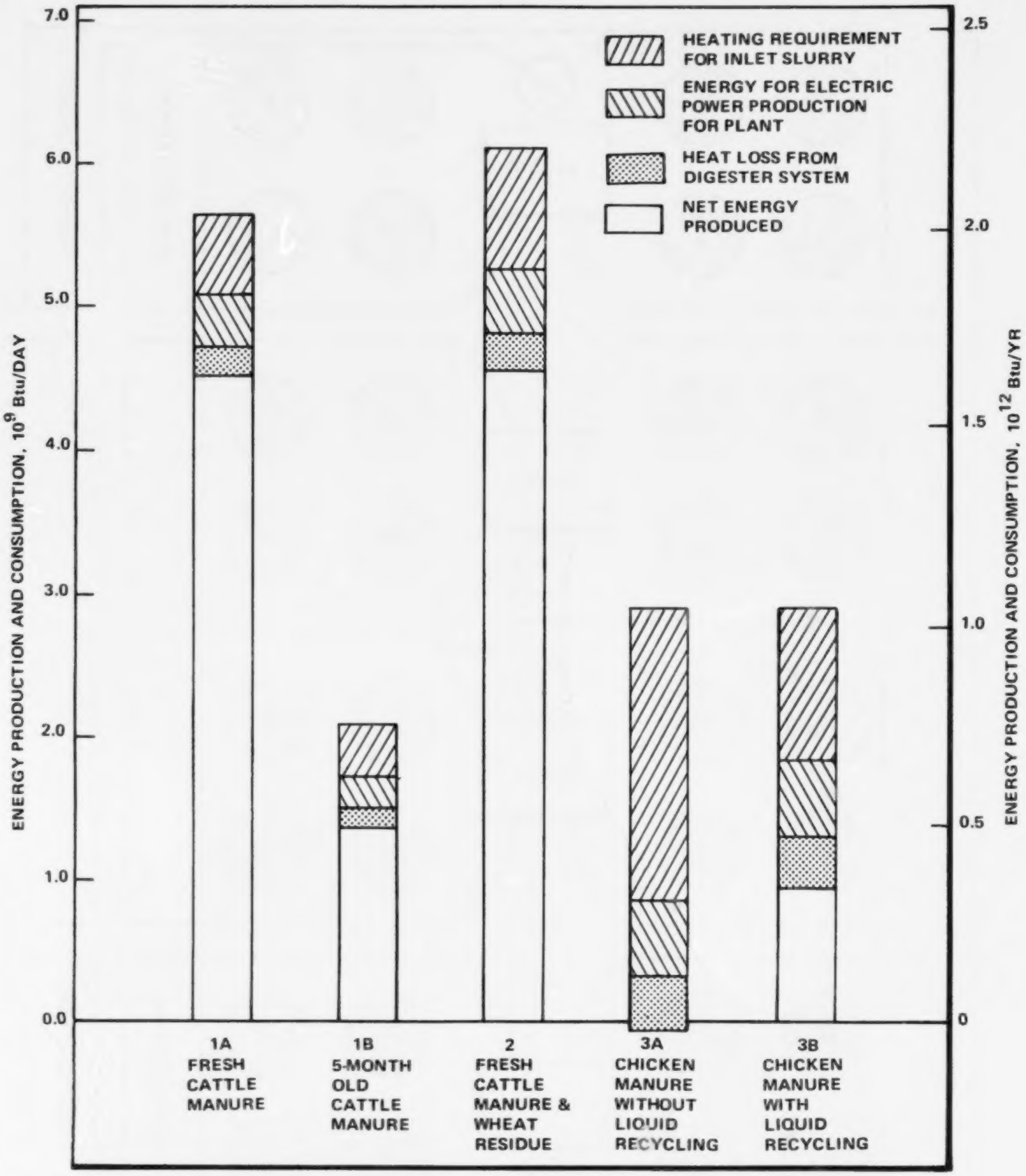
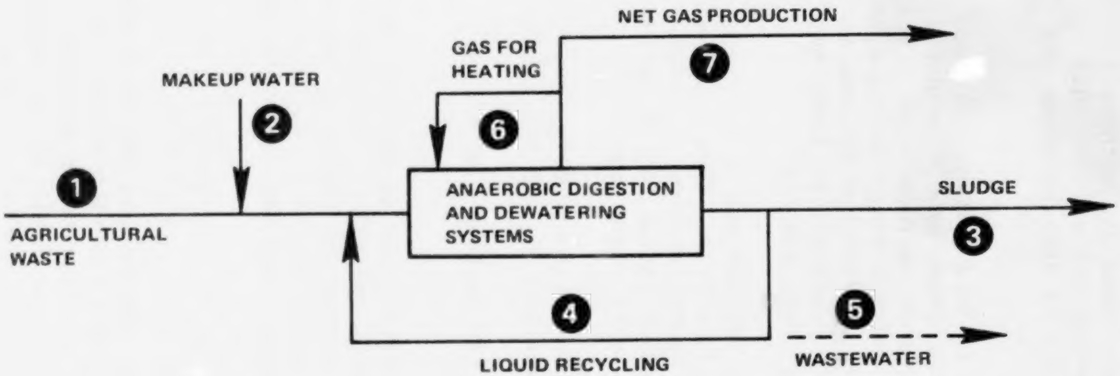


Figure 8. Energy production and consumption of anaerobic digestion process using various agricultural wastes as digester feed.



	❶ Agricultural wastes		❷	❸ Sludge		❹	❺	❻	❼ Net gas production		
										CH_4	CO_2
Agricultural wastes	Solids (lb/d)	Water (lb/d)	Makeup water (lb/d)	Solids (lb/d)	Water (lb/d)	Water recycled (lb/d)	Wastewater (lb/d)	Gas for heating (10^9 Btu/d)	(10^9 Btu/d)	(10^6 scf/d)	(10^6 scf/d)
Cattle manure (fresh)	2.20×10^6	0.88×10^7	0	1.35×10^6	0.41×10^7	1.10×10^7	0.47×10^7	0.74	4.83	5.03	2.71
Cattle manure (5-month collection cycle)	1.41×10^6	0.14×10^7	0.21×10^7	1.18×10^6	0.35×10^7	0.92×10^7	0	0.48	1.56	1.63	0.88
Cattle manure (fresh) and wheat residue	2.20×10^6 1.10×10^6	0.89×10^7	0	2.33×10^6	0.70×10^7	2.08×10^7	0.19×10^7	1.12	4.93	5.14	2.77
Chicken manure (without liquid recycling)	3.08×10^6	0.31×10^7	3.78×10^7	2.60×10^6	0.78×10^7	0	3.31×10^7	2.40	0.45	0.47	0.25
Chicken manure (with liquid recycling	3.08×10^6	0.31×10^7	0.47×10^7	2.60×10^6	0.78×10^7	3.31×10^7	0	1.42	1.43	1.49	0.80

Figure 9. Simplified material balances.

Manure and solid products are stored on sloped concrete storage areas; the runoff is collected for slurry makeup water. It has been assumed that the systems for cases 1B and 3B can be designed without any liquid discharge because an adequate system blowdown is achieved by disposing of a solids cake containing 75% water from the vacuum filters. For cases 1A and 2, with a fresh manure feed at 20% solids, wastewater streams are produced as indicated in the material balances for the five cases shown in Figure 10 (based on 1 lb of dry solids input for each case). Case 3A, without liquid recycling also produces a relatively large wastewater stream, but this alternative is not considered economically feasible by SRI, based on the system energy balances.

Cases 1A, 1B, and 2 are for a plant located in Weld County, Colorado. As indicated from the data in Table 15, evaporation ponds may be used for liquid disposal so that there would be no discharge to surface water. While evaporation ponds could produce odor problems at certain times and be a source of ammonia and H_2S, photosynthetic organisms could oxidize the H_2S and minimize its release. This water effluent might be used to irrigate the land, but dilution water may be required because of the high salt content.

This study has assumed that the entire solid residue can be sold or disposed of free F.O.B. plant gate as a fertilizer product. This disposal technique is planned for the proposed commercial installations. A credit might be given for reducing the volume (and pollution potential) of solid waste, but in this analysis we have assumed zero solid waste generated.

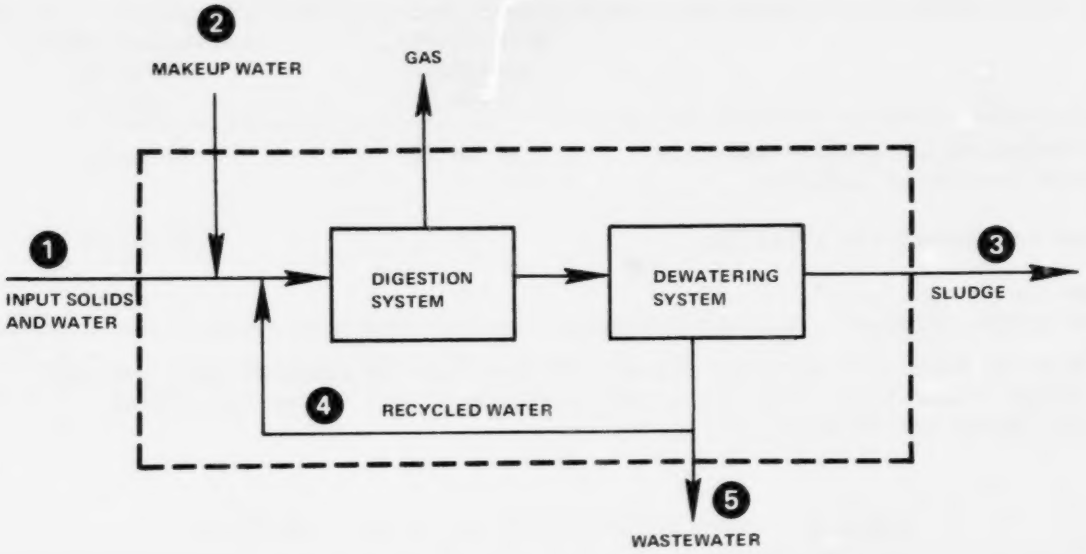
In our plant battery limits we did not include a gas-cleaning facility to upgrade the gas to pipeline quality (dehydration and CO_2 and H_2S removal).

For a discussion of the pesticide residues, see section 6 of this report.

We have assumed that all heavy metals are precipitated as sulfides and are contained in the solids cake from the dewatering operation. Nutrients are entirely contained in the solids product, in either the liquid or solid phases of that product for cases 1B and 3B. For cases 1A and 2, where wastewater is produced, some nutrients are discharged from the system to the evaporation ponds.

ENVIRONMENTAL ANALYSIS

In the environmental analysis of agricultural residue conversion systems, the gas-producing processes are compared with coal gasification (SNG); the direct firing or cofiring cases are compared with electric power generation in fossil fuel-fired power plants. The format, shown in Table 16, is similar to that of the Council on Environmental Quality because impacts are considered from the resource extraction through to the conversion plant. Because the typical energy output quantities differ in a coal conversion plant and agricultural residue processing plant, the comparison is based on common units. We present the results as units per million of net Btu produced. In calculating the net energy output for the gas-producing processes, we



	①*		②	③		⑤
	Input solids		Makeup	Output solids		
Case	Dry solids (lb/d)	H_2O (lb/d)	H_2O (lb/d)	Dry solids (lb/d)	H_2O (lb/d)	Wastewater (lb/d)
1A	1	4	0	0.614	1.842	2.158
1B	1	1	1.511	0.837	2.511	0
2	1	2.7	0	0.706	2.118	0.582
3A†	1	1	12.285	0.844	2.532	10.753
3B	1	1	1.532	0.844	2.532	0

	1A	1B	2	3A	3B
*Assumptions for percent solids in feed:	20	50	27	50	50
Assumptions for percent solids in product:	25	25	25	25	25

†No internal recycle liquid.

Figure 10. Material balance.

TABLE 15. PRECIPITATION AND EVAPORATION RATES[*]

	Weld County, Colorado (in.)	Washington County, Arkansas (in.)
Average annual evaporation rate from open water surfaces	34 to 36	44 to 46
Average annual precipitation	15	40 to 50
Average annual runoff	< 1	10 to 15

[*] Western Texas and Oklahoma (where CRAP facility is planned) have average annual evaporation rates from open surfaces of >60 inches and annual precipitation rates of <25 inches.

TABLE 16. SAMPLE ENVIRONMENTAL ANALYSIS WORKSHEET

Impact		Resource extraction	Onsite processing or storage	Transport to conversion plant	Conversion plant
Land disruption and use	Acres/10^9 Btu/day output				
Water pollution					
Input	(gal/10^6 Btu)				
Output	(gal/10^6 Btu)				
Ammonia	(lb/10^6 Btu)				
Phosphorous	(lb/10^6 Btu)				
Salts	(lb/10^6 Btu)				
Metals	(lb/10^6 Btu)				
Pesticides	(lb/10^6 Btu)				
Air pollution					
NO_x	(lb/10^6 Btu)				
SO_x	(lb/10^6 Btu)				
H_2S	(lb/10^6 Btu)				
Particulates	(lb/10^6 Btu)				
Pesticides	(lb/10^6 Btu)				
Organisms					
Solid waste total	(lb/10^6 Btu)				

assume that purchased electric power is generated by coal-fired power plants (CFPP) and that no loss in transmission occurs; a plant thermal efficiency of 40% is assumed. The Btu equivalent of the fuel burned to produce the electric power is subtracted from the energy output to calculate the net output. The pollutants generated in the production of electric power for use at the gas-production facilities are shown on the emissions comparison graphs, along with the emissions from the gas production facilities. The analysis for the digestion cases is based on a coal-fired power plant burning 0.8% sulfur coal with flue gas desulfurization to reduce SO_2 emissions to 0.83 lb $SO_2/10^6$ Btu output.

The assumptions and data used for the analysis are summarized in Appendix B. Resource requirements (land, water) and emissions are tabulated for each process. The results of the analysis are illustrated in Figures 11 through 16.

POTENTIAL PROCESS PROBLEMS

The potential process problems for the anaerobic digestion processes discussed in Appendix A include:

- Ammonia toxicity (may require recirculating gas treatment or liquid recycle treatment in algae treatment lagoon)
- H_2S and NH_3 control for thickener and vacuum pump exhaust gases (iron oxide or activated carbon bed, acid scrubbing)

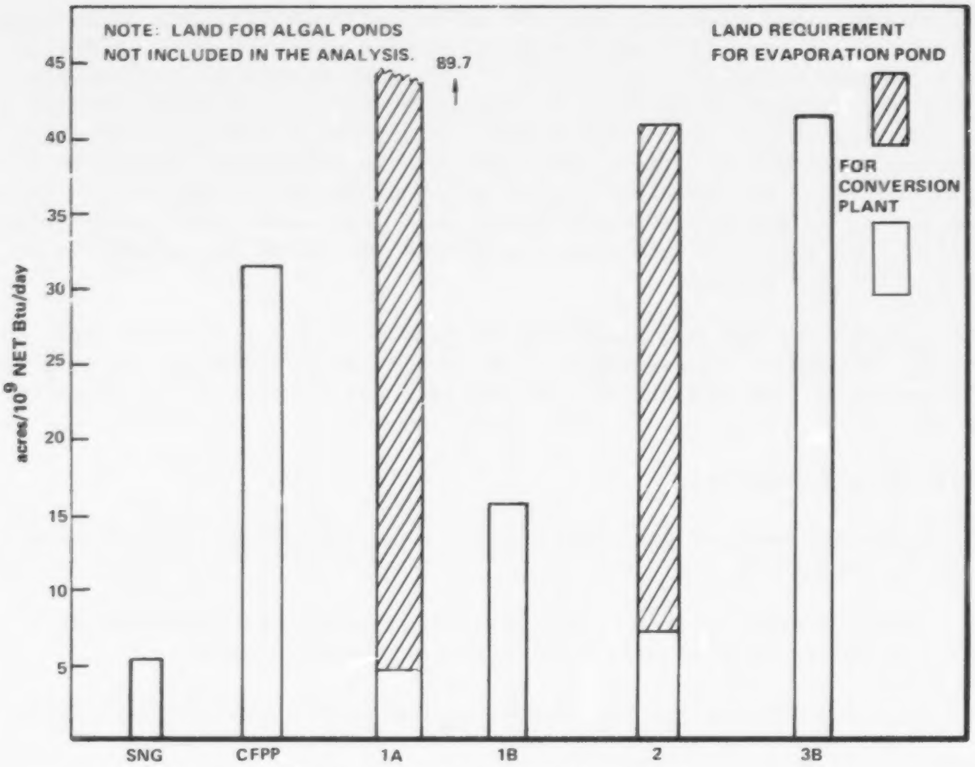
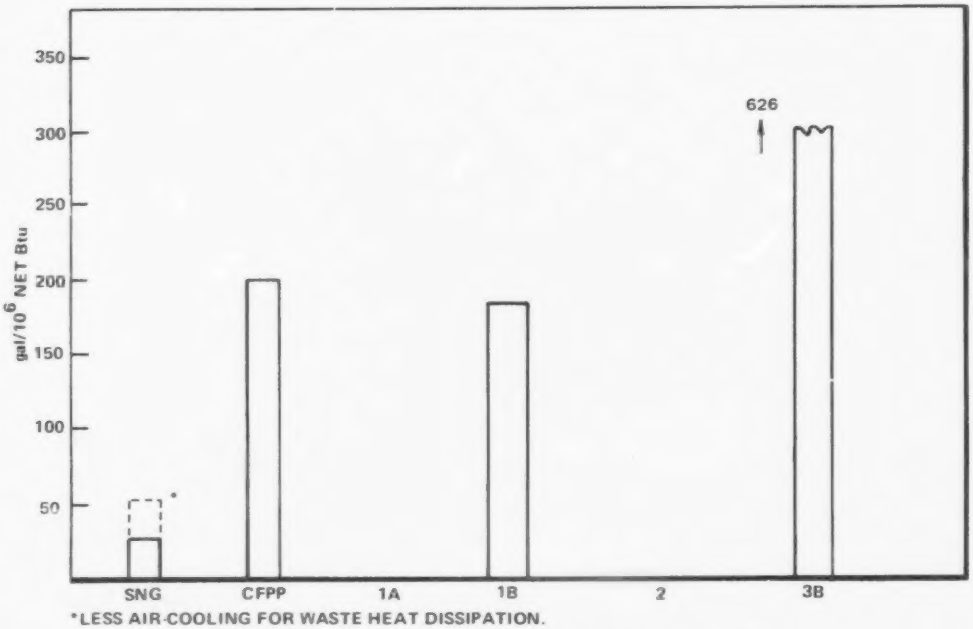


Figure 11. Land requirements.



*LESS AIR-COOLING FOR WASTE HEAT DISSIPATION.

Figure 12. Input water requirements.

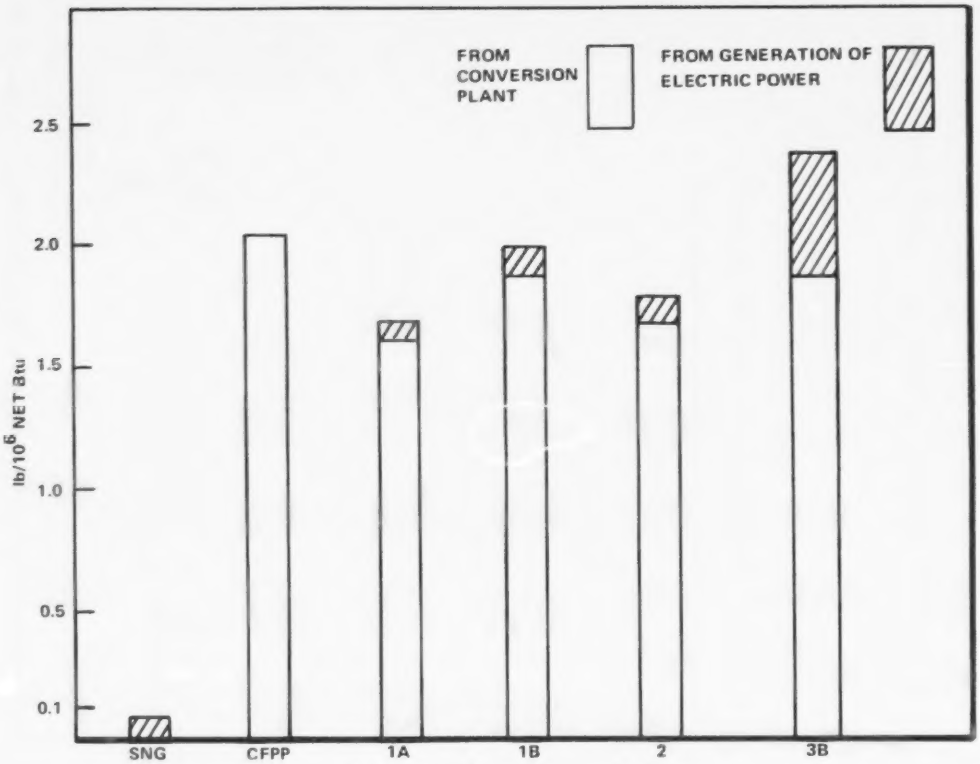


Figure 13. NO_x emissions.

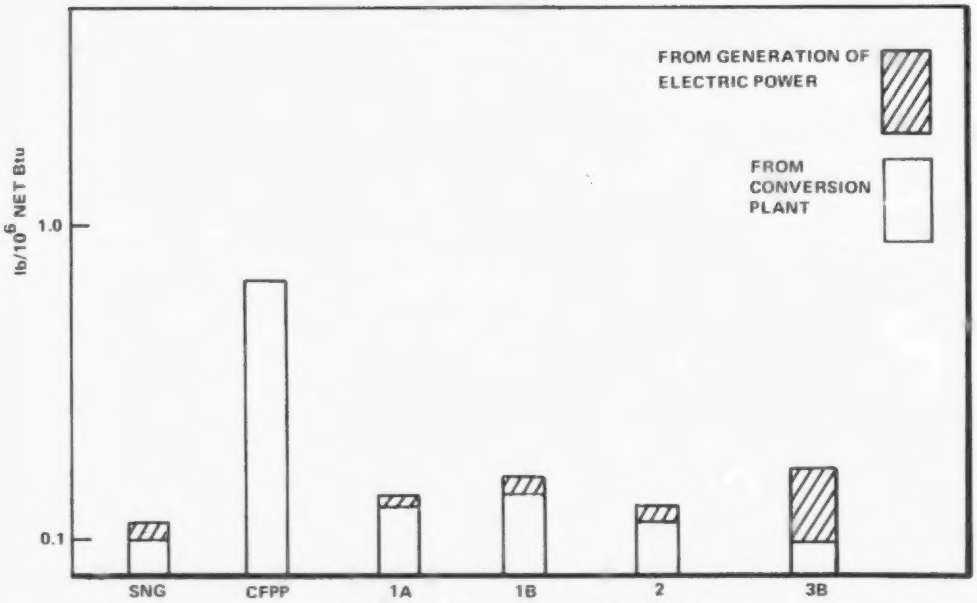


Figure 14. SO_2 emissions.

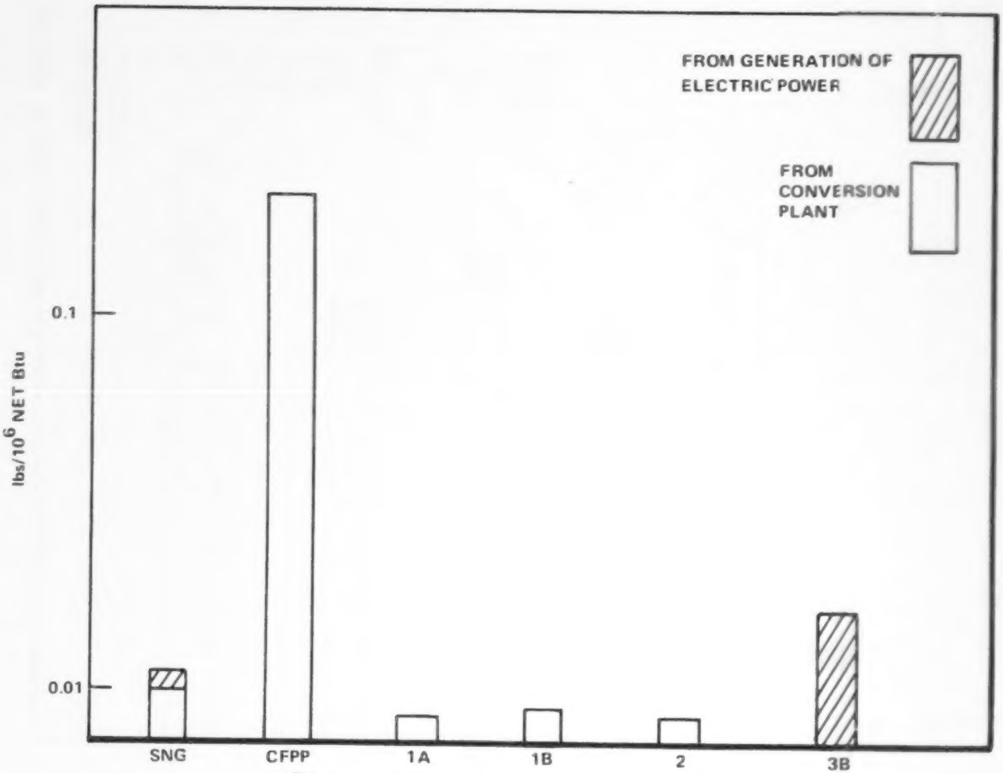


Figure 15. Particulate emissions.

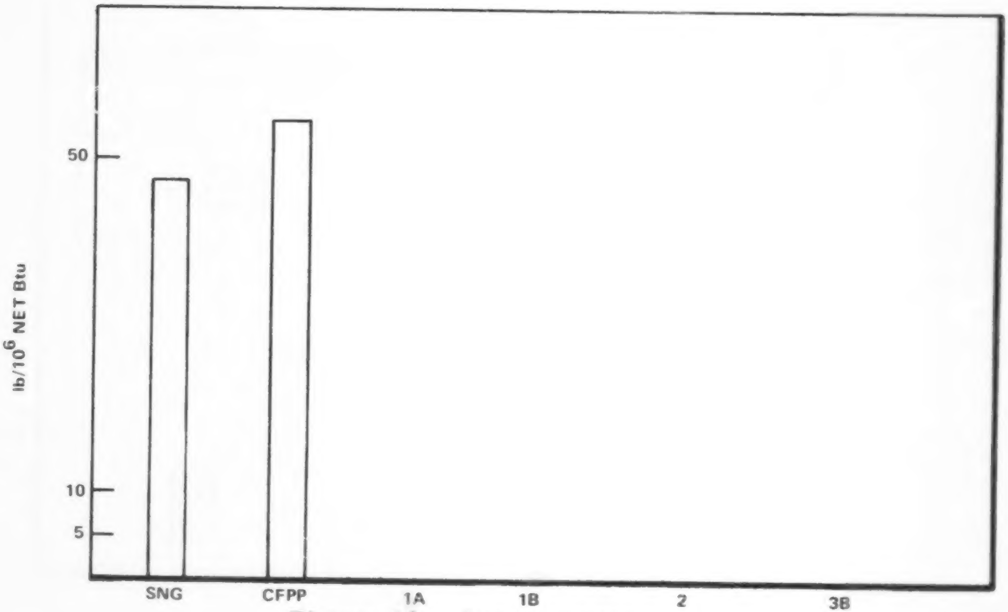


Figure 16. Solid wastes.

SECTION 9

DIRECT FIRING OF RESIDUE

INTRODUCTION

Direct firing of many types of wood waste and sugarcane byproducts such as bagasse is a well-established technology. Wood wastes such as sawdust, bark, shavings, and hog fuel are increasingly being used in lumber mills and paper mills as a source of energy. A substantial effort is being made in the lumber industry to improve this technology so as to increase efficiency and meet environmental control regulations. In the sugarcane industry, the extracted cane, called bagasse, is burned in boilers to supply heat and electrical power to the sugar mill. Sugar mills are generally energy self-sufficient, although fuel oil is sometimes used as a backup fuel or for startup.

The two cases of direct firing technology discussed here use logging residue and sugarcane trash as feedstocks. Logging residue is that residue that, up to now, has been left in the forest. This residue includes tops, limbs, stems, saplings, dead and rotting trees, undesirable trees, and possibly even stumps and roots. Sugarcane trash is defined as the leaves, tops, and field trash that are currently not desirable to collect. At present, this trash is destroyed in a flashfire burn of the field the day before the harvest of the cane.

PROCESS DESCRIPTION

Direct firing generally includes the following steps:

- Harvesting or collecting of the material
- Transportation to the plant
- Feed preparation (cleaning, drying, size reduction, etc.)
- Feeding to and combustion in a boiler
- Heat recovery as steam used for process or building heat or for electric power generators
- Cleanup of stack gas and disposal of ash residue

PROCESS FEEDS

Forestry Residue

Forestry residue is discussed in section 7 of this report. Basically, wood waste is sulfur-free and lower in ash than coal. The waste is high in moisture, however, and the moisture content is highly variable. The following elemental analysis has been assumed for this study:

Element	Dry wt %
Carbon	49.6
Hydrogen	5.7
Oxygen	43.7
Nitrogen	0.2
Other	0.8

Moisture is assumed to be 50% wt (wet basis).

Sugarcane Residue

At present, sugarcane residue (leaves, tops, etc.) is burned in the field before cane harvesting. To date, collection of this material has proved uneconomical, since the energy value recovered does not offset the added cost of collection. Sugarcane has the following elemental analysis (dry basis):

Element	Reported range (% wt)	Value used (% wt)
Carbon	43 to 47	45
Hydrogen	5.4 to 6.6	6.0
Oxygen	45 to 49	47
Ash	1.5 to 3.0	2.0
		100

The moisture content is highly variable, depending on the exact makeup of the trash and the harvesting time, but we assume the moisture content to be 50% wt (wet basis).

LAND DISRUPTION FROM CONVERSION PROCESS

There are several options in the use of logging residue for direct firing or cofiring technology. Two primary uses are steam or heat generation in industrial plants (such as lumber drying or paper and pulp mills), or in electric utility power plants. In either case, the *net* land disruption in using logging residue, as opposed to alternative fuels, is mainly the storage facility. Since both cases use a large combustion unit, the size and land usage should be about the same.

If all 1,000,000 tons/yr of logging residue were collected, chipped, and sent to a central plant for direct combustion, an area equal to 30 days' storage would be needed. If a pile 30 ft high contains 100,000 tons (assuming a bulk density of 20 lb/ft^3), the area required would be 330,000 sq ft, or about 8 acres. Considering access area and operating room, about 14 acres should be allowed.

Disposal of ash from a 3000 ton/day combustion plant requires about 0.2 acre/yr, or a total of 4 acres for a 20-yr project life.

Total land disruption, therefore, is:

	Acres	
Collection	1	
Storage	14	
Ash disposal	4	(0.2 acre/yr)
Total	19	

The 3000 ton/day plant ($1x10^6$ ton/yr) producing 4000 Btu/lb or 8,000,000 Btu/ton produces $8x10^6x10^6 = 8x10^{12}$ Btu/yr, gross. Thus, 19 acres/ $8,000x10^9$ Btu/yr = 0.0002 acre/10^9 Btu/yr. If a 30% efficiency is realized in the combustion, then 0.0006 acre/10^9 Btu/yr is used.

DIRECT COMBUSTION OF FORESTRY RESIDUE

The forestry residue collected and chipped in the field is transported to the point of use. (The collection, chipping and transportation are discussed elsewhere.) The final steps in the process are grinding, drying, and combustion. The first two steps may not be necessary, depending on the size chip produced in the field and the moisture content.

Final Grinding, Drying, and Feeding

The chips are transported from the storage pile to the power plant. A final reduction in size is probably needed to generate a sawdust-like feedstock. This material may or may not need drying, but present thinking is to use a dryer to increase the steam-generating capacity of the boilers. The particulate emissions from the final grinding can be controlled by drawing the particulate-laden air directly into the furnace.

Several types of dryers could be used, depending on the requirements of the plant. The chips could be dried before final grinding or the fine material could be dried in a fluid bed on a transport-type dryer. The particulate emission is minimized if the larger chips are dried, but a higher rate of drying is achieved if the fine feedstock is dried. This decision must be made by the design engineers and appropriate steps taken to minimize particulate emissions.

Material Balance

To simplify the calculations in Table 17, we assume that the as-received wood is fed directly to the boiler. The total feed is 3000 tons/day or 125 tons/hr (250,000 lb/hr). The wood is assumed to contain 8000 Btu/lb (dry basis). Actually, several boilers would be operated in parallel to process this amount of feed. The units use 40% excess air and produce a total of $1x10^6$ lb of steam/hr at 600 psig and 900°F.

On this basis, $535x10^6$ Btu/hr are produced as high-pressure steam, while $465x10^6$ Btu/hr are lost to the stack gases. Based on reported data for wood combustion, about 1250 lb/hr each of CO and NO_x are formed from the combustion; with reasonable collection efficiency in a dry cyclone (80%), only 100 lb/hr of particulates would be emitted. The solid waste from the boilers is mainly ash, totaling about 400 lb/hr.

TABLE 17. MATERIAL BALANCE

	Flow (10^3 lb/hr)				
	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5
Composition					
Wood (50% moist)	250				
Air		2238.4			
Steam (600 psig, 900°F)			365.8		
Flue gas (400°F)				2488.4	
Ash				0.1	0.4
Elemental and component balance					
C	62	-	-	-	-
H	7.2	-	-	-	-
O	54.6	235.0	-	67.1	-
N	0.25	884.2	-	884.2	-
S	0	-	-	-	-
Ash	0.5	-	-	0.1	0.4
CO	-	-	-	1.25	-
CO_2	-	-	-	227.3	-
NO_x	-	-	-	1.25	-
H_2O	125	-	365.8	189.8	-
SO_2	-	-	-	0	-
Btu	$1x10^9$	0	$0.535x10^9$	$0.465x10^9$	-

Emissions

Emissions are summarized in Table 18. The combustion process emits CO and oxides of nitrogen. Proper design of the combustion chamber and proper operation of the boiler minimize these emissions, but they still are present. Sulfur dioxide emissions are quite low, the actual value depending on the sulfur content of the wood waste used. In the wood waste used for this material balance, no sulfur was reported. However, some wood contains amounts of sulfur up to 0.1% wt (wet basis), which gives a SO_2 emission of about 0.25 lb $SO_2/10^6$ Btu.

Particulates could be quite high if uncontrolled. Values as high as 8 to 10 lb particulates/10^6 Btu are possible in uncontrolled systems burning high concentrations of wet feed and bark.

Predrying of the feedstock greatly reduces the particulate emission from the boiler, but may necessitate a particulate removal step at the dryer. Both

TABLE 18. ENVIRONMENTAL IMPACTS OF DIRECT COMBUSTION OF LOGGING RESIDUE, HUMBOLDT COUNTY, CALIFORNIA

Impact		Resource extraction	Onsite processing or storage	Transport to conversion plant	Conversion plant
Land disruption and use	Acres/ 10^9 Btu/ yr/output	<0.001	<0.001		<0.001
Water pollution					
Input	(gal/10^6 Btu)				175
Output	(gal/10^6 Btu)				0
Wasteheat	(Btu/10^6 Btu)				-
Ammonia	(lb/10^6 Btu)				-
Phosphorus	(lb/10^6 Btu)				-
Salts	(lb/10^6 Btu)				-
Metals	(lb/10^6 Btu)				-
Pesticides	(lb/10^6 Btu)				-
Air pollution					
NO_x	(lb/10^6 Btu)		0.02	0.01	0.7
SO_x	(lb/10^6 Btu)		0.002	0.002	0
H_2S	(lb/10^6 Btu)		-	0	0.1
Particulates	(lb/10^6 Btu)		0.002	<0.001	0
Pesticides	(lb/10^6 Btu)		-	0	-
Hydrocarbons	(lb/10^6 Btu)		0.002	0.003	0
CO	(lb/10^6 Btu)		0.007	0.02	0.25
Organisms			-	0	0
Solid waste total	(lb/10^6 Btu)		-	0	0.7

baghouses and dry scrubbers show excellent efficiency in removing particulates from wood waste fired boilers.[7] Removal efficiencies for baghouses are 90% and for dry scrubbers 87%. The baghouse requires a much lower pressure drop (3 inches of water) compared to the dry scrubber (14 inches of water). Total particulate matter at the outlet of these tests was between 0.033 and 0.061 grain/scf, or less than 0.1 lb particulates/10^6 Btu output.

Therefore, while the potential particulate emissions are quite high, with proper design, the actual emission should be well below the New Performance Source Standards for coal-fired power plants (0.1 lb particulates/10^6 Btu input).

DIRECT COMBUSTION OF SUGARCANE RESIDUE

Material Balance

Collected sugarcane trash is mixed with bagasse and fired in boilers at the sugar mills, as shown in Figure 17. A material balance sheet is presented in Table 19. This system makes better use of existing facilities than would building a central power plant. Additional boilers and generating capacity are added at each plant to accommodate the added feedstock.

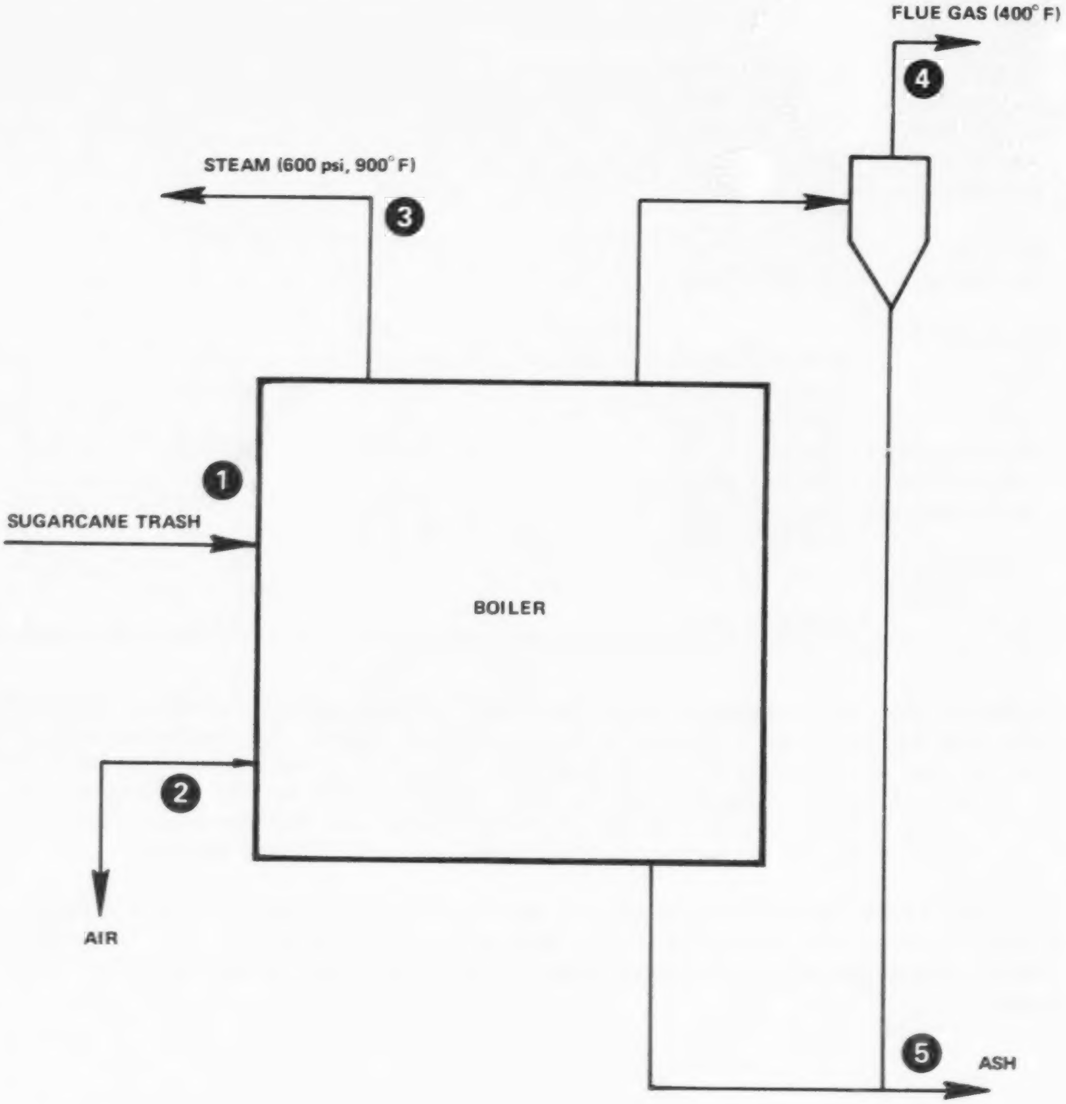


Figure 17. Direct firing of sugarcane trash.

TABLE 19. MATERIAL BALANCE FOR SUGARCANE TRASH COMBUSTION (tons/day)

	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5
Sugarcane trash	500				
Air		2016.5			
Flue gas				2515.5	
Ash				0.5	5
Steam			556		
Btu	3×10^9		1.625×10^9	1.375×10^9	
Elemental balance					
C	112.5			112.5	
H	15			15	
O	117.5	423.5		541	
N		1593		1593	
S	trace				
Ash/particulate	5			5.5[a,b]	5
H_2O	250		556	250	
CO				0.5[a]	
CO_2				412.5	
H_2O	250		556	385	
SO_2				0	
NO_x				0.5[a]	
O_2		423.5		121	
N_2		1593		1593	
Hydrocarbons				0.5[a]	

[a] Source: Reference 3.

[b] Uncontrolled; with controls, approximately 0.5 ton/day.

As with forestry waste, there is the option of drying the feedstock. The feed is chopped into small pieces, 2 inches (maximum) in diameter. Drying generates some particulates, but firing the undried cane trash may produce an equal amount. The real tradeoff is between the cost of a dryer and the cost of a larger boiler. The dried feed generates more energy per pound and thus requires a smaller boiler. However, the overall energy balance shows that the water is removed somewhere and this heat of vaporization is lost.

This analysis assumes that no dryer is used and that the sugarcane trash is fed as received. The emissions are summarized on Table 20. The main pollutant potentially emitted is the particulate at a rate of 22 lb/ton of feed or about 3.5 lb/10^6 Btu. However, all Florida sugar mills are now being equipped with wet scrubbers; present emissions from bagasse boilers are in the range of 0.05 to 0.1 lb/10^6 Btu.

TABLE 20. ENVIRONMENTAL IMPACTS, DIRECT COMBUSTION OF SUGARCANE TRASH[a]

Impact		Onsite processing or storage	Transport to conversion plant	Conversion plant
Land disruption and use	Acres/ 10^9 Btu/ yr output			0.011
Water pollution				
Input	(gal/10^6 Btu)			
Output	(gal/10^6 Btu)			
Wasteheat	(Btu/10^6 Btu)			
Ammonia	(lb/10^6 Btu)			
Phosphorus	(lb/10^6 Btu)			
Salts	(lb/10^6 Btu)			
Metals	(lb/10^6 Btu)			
Pesticides	(lb/10^6 Btu)			
Air pollution				
NO_x	(lb/10^6 Btu)			0.62
SO_x	(lb/10^6 Btu)			0
H_2S	(lb/10^6 Btu)			0
Particulates	(lb/10^6 Btu)			6.77 (0.62)
Pesticides	(lb/10^6 Btu)			0
Hydrocarbons	(lb/10^6 Btu)			0.62
CO	(lb/10^6 Btu)			0.62
Organisms				-
Solid waste total	(lb/10^6 Btu)			6.6

[a]Source: Reference 8.

Land Disruption - Conversion Process

The major impacts on land usage are the storage area for the cane trash and the ash disposal area. The ash may be returned to the fields for its fertilizer value (indeed, in the present field burning, that is exactly what is done), but provision for interim storage of ash is made. Also, the cane is harvested over about a 6-month period, and provision for storage must be made for at least a 6 months' supply. If 1,000,000 tons/yr were collected, the storage area should be able to contain a minimum of 500,000 tons. Two options are available: (1) prepare the cane trash for combustion at the time of harvest (i.e., grinding, drying, etc.) and store the resultant boiler feed material in silos; (2) prepare the feed as needed and store the raw trash in large piles. The latter method is assumed as it uses a maximum amount of land, even though there may be severe technical and operational problems (rotting, moisture, rodents, etc.).

Assuming a bulk density of semicompacted leaves and trash to be 20 lb/ft, a storage area of 50,000,000 ft^3 is required for 500,000 tons. If the material can be stored in piles 20 ft high, 2,500,000 ft^2 or 57 acres would be required. Allowing another 10 acres for equipment access, a minimum of 67 acres is required. Considering the heat content of 6x10^{12} Btu/yr, the land use factor is 0.011 acre/10^9 Btu.

Collected and Fired Cane Trash Emissions Compared to Open Field Burning

To evaluate properly the environmental effects of collecting and firing cane trash in a boiler, the alternative practice of flash burning in the field must be considered. US EPA data[9] show that the following emissions are created when cane trash and weeds are burned in the field:

Composition	lb/acre
Particulate	225
Carbon monoxide	1500
Hydrocarbons	300
Nitrogen oxide	30

Based on 15 tons/acre, and 6x10^6 Btu net heat per ton of trash, the emissions are:

Composition	lb/10^6 Btu
Particulate	2.5
Carbon monoxide	16.7
Hydrocarbons	3.3
Nitrogen oxide	0.3

In comparison, the total emissions from collecting, processing, and combustion of sugarcane trash in a boiler are:

Composition	lb/10^6 Btu	
Particulate	0.62	(with controls)
Carbon monoxide	0.65	
Hydrocarbons	0.624	
Nitrogen oxide	0.64	
Sulfur dioxide	0.002	

Obviously, collection and boiler firing is both a more productive method of disposal, yielding valuable energy, and environmentally more desirable. Other items to consider that are beyond the scope of this report are:

- The possible pesticide emissions from field burning
- The positive effects of field burning on disease and rodent control
- The effects on product yield
- The overall economics

COFIRING WITH COAL IN A STOKER-FIRED BOILER

The concept of using refuse and agricultural waste as a fuel is not new in the United States, nor for that matter, in Europe. Studies have been made to determine the practicality of using such materials as fuels for stoker-fired boilers. Replacing part of the coal with agricultural waste appears a viable concept, if the pollution factors are not greater or potentially more harmful than that of coal alone, and if collection costs are reasonable. (See Figure 18 for a flowchart of this process.)

At the three sites of this study, the crop residue comes from corn, barley, wheat, and sunflower. This includes straw, chaff, and leaves.

Process Description

Stokers are designed to feed coal uniformly onto a grate within the furnace and to remove ash residue. Most mechanical stokers can be classified in three main groups:

- Overfeed: chain grate; traveling grate; vibrating and oscillating grate
- Spreader
- Underfeed

Supplementing coal with agricultural waste involves the following steps:

- Harvesting or collecting the material
- Transporting material to the plant
- Preparing the feed (drying, size reduction, etc.)
- Storing
- Mixing with coal
- Feeding to and combusting in the boiler
- Recovering heat
- Cleaning up of stack gas and disposal of ash residue

Collection

This study assumes that, in all cases, the wastes are harvested at the same time as the food crop. The wastes are then separated from the food crop and moved to the transportation unit.

Process Feeds

Barley--

Barley refuse is considered for use with lignite in the Traill, North Dakota area, along with wheat and sunflower wastes. The mix is:

Waste	Percent
Wheat	65
Barley	25
Sunflower	10

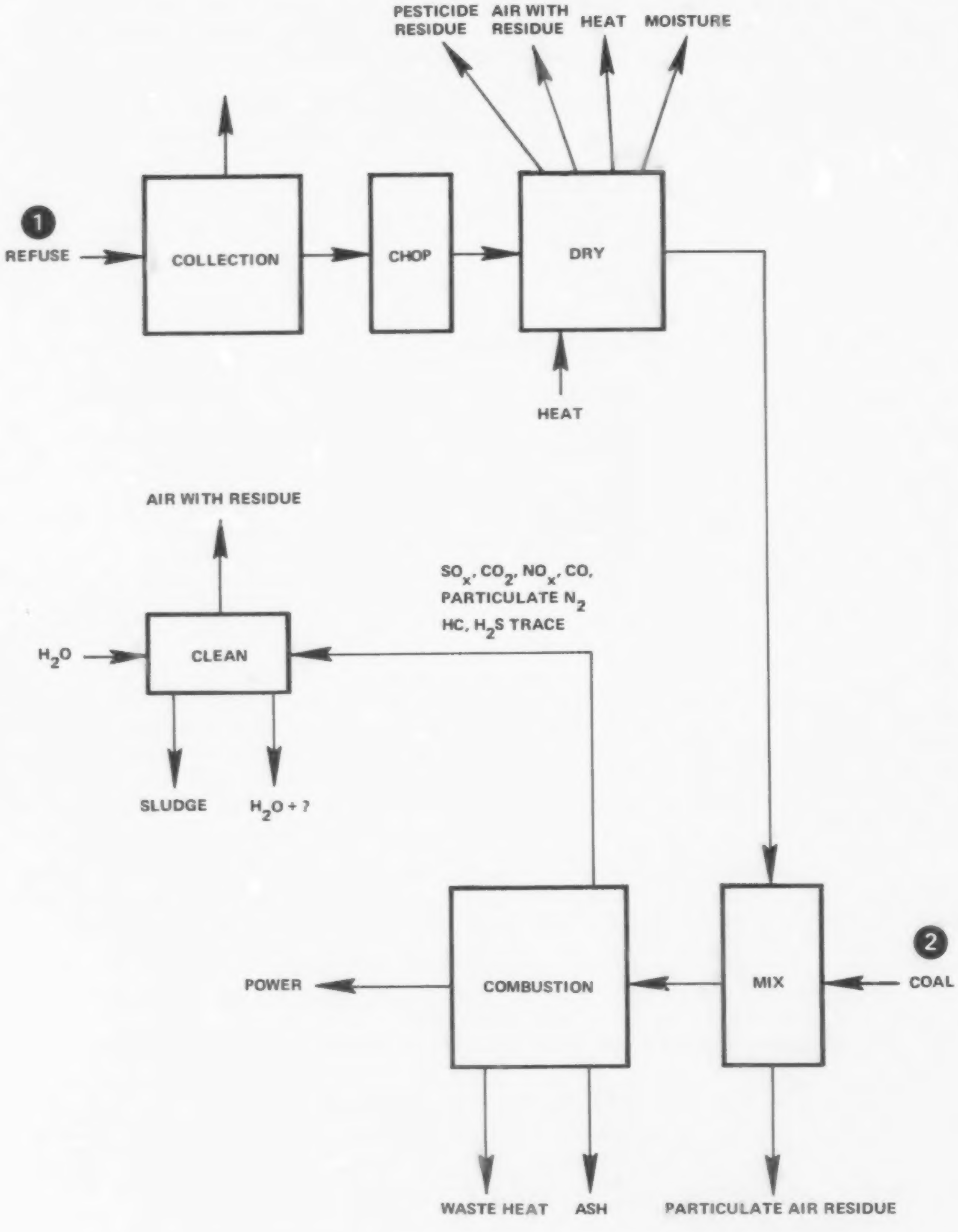


Figure 18. Cofiring with coal in a stoker-fired boiler.

This mixture would supplement the lignite now used. Approximately 6,000,000 tons/yr of assorted crop waste are available; case studies were prepared using 0, 25, and 50% waste-to-lignite ratios.

Barley straw is approximately 10 to 15% moisture and 5.5% ash. For this study, the ultimate analysis of the material was assumed to be as follows:

Element	Dry wt %
Carbon	43
Hydrogen	6
Nitrogen	0.5
Oxygen	5.5

The ash contains the following elements:

Element	Dry wt %
Calcium	0.35
Chlorine	0.68
Iron	0.033
Magnesium	0.13
Manganese	0.0017
Phosphorus	0.10
Potassium	1.88
Sodium	0.14
Sulfur	0.17

Wheat--

Wheat waste is also considered for use with lignite in the Traill, North Dakota area with barley and sunflower waste, and in the Marshall, Missouri area with corn waste and corn. The mix considered is given under barley. Approximately 6,000,000 tons/yr of assorted crop waste are available in North Dakota; case studies were prepared using 0, 25, and 50% waste-to-lignite ratios.

In the Marshall, Missouri area approximately 1,000,000 tons/yr of wheat and field corn waste are available. Case studies were prepared using 0, 25, and 50% waste-to-coal ratios. The wheat and corn mix considered was 50% wheat and 50% corn.

Wheat waste is approximately 30% moisture and has about 4.3% ash.

The ultimate analysis of wheat waste was assumed to be as follows:

Element	Dry wt %
Carbon	43.0
Hydrogen	4.2
Nitrogen	4.5
Oxygen	44.0
Ash	4.3

The ash contains the following elements:

Element	Dry wt %
Calcium	0.16
Chlorine	0.33
Copper	trace
Iron	0.017
Magnesium	0.12
Manganese	0.006
Phosphorus	0.08
Potassium	0.67
Sodium	0.14
Sulfur	0.10

We assume that the waste is collected at the time of harvest and that the waste is separated from the food crop mechanically before it is moved to the transportation unit.

Sunflower--

Sunflower waste is considered for use with lignite, wheat, and barley in the Traill, North Dakota area. The mix is:

Waste	Percent
Wheat	65
Barley	25
Sunflower	10

Approximately 6,000,000 tons/yr of the assorted crop waste (barley, wheat, sunflower) are available; case studies were prepared using 0, 25, and 50% waste-to-lignite ratios.

Sunflowers have 50% moisture and about 6% ash. The elemental analysis used in this study was assumed to be as follows:

Element	Dry wt %
Carbon	48.4
Hydrogen	7.0
Nitrogen	3.6
Oxygen	35.0
Ash	6.0

The ash contains the following elements:

Element	Dry wt %
Calcium	1.72 - 2.2
Magnesium	0.09 - 0.64
Manganese	0.11
Phosphorus	0.20 - 0.56
Potassium	2.92 - 5.0
Sulfur	0.04

Collection of the sunflower waste is assumed to be the same as barley and wheat.

Corn--

Corn waste is considered for use in both the Marshall, Missouri and Sibley, Iowa areas. In the Missouri region, there are available approximately 1,000,000 tons/yr of corn and wheat waste; in the Iowa area, approximately 4,500,000 tons/yr of corn are available. Case studies were prepared using 0, 25, and 50% corn waste-to-coal ratios.

Corn stalks and leaves are approximately 50% moisture and have about 4.5% ash.

The ultimate analysis of corn waste was assumed to be as follows:

Element	Dry wt %
Carbon	43.5
Hydrogen	6.0
Nitrogen	1.5
Oxygen	44.5
Ash	4.5

The ash contains the following elements:

Element	Dry wt%
Calcium	0.23
Potassium	0.92
Magnesium	0.18
Phosphorus	0.20
Iron	0.08
Silicon	1.17
Aluminum	0.11
Chlorine	0.14
Manganese	0.035
Sulfur	0.18

Coal and Lignite--

The coals used in this study were North Dakota lignite and Illinois No. 6 coal. For the purpose of this study, the following fuel mixes were used:

- Traill, North Dakota
    - Lignite
    - Refuse: wheat 65%, barley 25%, sunflower 10%
- Marshall, Missouri
    - Illinois No. 6 coal
    - Refuse: 50% wheat, 50% corn
- Sibley, Iowa
    - Illinois No. 6 coal
    - Refuse: 100% corn

Lignite has a moisture content, after drying, of 11.4% and an ash content of 9.6%. Illinois No. 6 coal has a moisture content, after air drying, of 8.4% and an ash content of 10.5%. The ultimate and ash analyses are as follows:

	Illinois No. 6 coal	North Dakota lignite
Hydrogen	5.4	5.1
Carbon	69.3	57.9
Nitrogen	1.2	0.8
Oxygen	15.5	25.8
Sulfur	3.5	1.2

Ash analyses for lignite and coal are as follows:

	Illinois No. 6 (total ash 10.5%)	Mercer lignite (total ash 9.6%)
SiO_2	51.7	23.8
Al_2O_3	15.7	10.5
Fe_2O_3	16.3	10.1
TiO_2	0.6	0.6
P_2O_5	0.06	0.27
CaO	8.9	16.6
MgO	0.8	5.1
Na_2O	0.5	8.2
K_2O	2.0	0.6
SO_3	2.8	23.5

Material Balance

Tables 21 through 25 summarize the material balance and air emission at the three sites; these are then compared with coal-only firing. As expected, the sulfur emissions are lower due to the lower sulfur concentration in the feedstocks. No data for NO_x emissions were found, so no increased emissions were considered. However, we do feel that the NO_x emissions might be lower due to the lower temperatures in the boiler. In all cases the CO concentrations increased with increasing agricultural residue in the feed. This is due mainly to the extra combustion required of drying feedstocks to give a comparable output energy. Particulates also increase, due mainly to a low collection efficiency on the residue dryer (80%) compared to the higher efficiency of the particulate collection devices on the boiler (98%). In the case of lignite firing in Traill, North Dakota, the total hydrocarbons actually decrease with increasing agricultural residue in the feed. This is due to the dilution effect of the residues. Agricultural residues emit less hydrocarbons on combustion than does lignite. However, the reverse is true in the case of Illinois No. 6 coal. The residues actually emit more hydrocarbon than does coal.

TABLE 21. MATERIAL BALANCE
(tons/day)

Site	Feed refuse (%)	Coal in	Refuse in	SO_2[a] out	Ash out	Particulate out[a]	CO out	HC out	NO_x out
Traill, N. Dakota	50	211	242	6.7	28	9.8	0.57	0.14	1.2
	25	311	119	9.5	34	11.8	0.49	0.17	1.2
	0	408	-	12	39	13.7	0.41	0.20	1.2
Marshall, Missouri	50	189	426	14	31	16.9	0.73	0.092	5.3
	25	274	207	20	34	20.7	0.45	0.072	5.3
	0	355	-	25	37	24.2	0.17	0.053	5.3
Sibley Iowa	50	16.9	43.4	1.3	2.8	1.8	0.089	0.030	0.23
	25	24.2	20.7	1.7	3.0	2.0	0.055	0.022	0.23
	0	30.9	-	2.2	3.2	2.1	0.031	0.015	0.23

[a] Uncontrolled

TABLE 22. EMISSIONS
($lb/10^6$ Btu)

Site	Feed refuse (%)	SO_2[a]	Particulate[b]	NO_x	CO	HC	Pesticides
Traill, N. Dakota	50	1.2	0.37	1.4	0.66	0.16	0
	25	1.7	0.34	1.4	0.57	0.20	0
	0	2.1	0.32	1.4	0.48	0.23	0
Marshall, Missouri	50	1.7	0.45	4.3	0.59	0.075	0
	25	2.4	0.42	4.3	0.37	0.059	0
	0	3.1	0.39	4.3	0.14	0.043	0
Sibley, Iowa	50	1.9	0.56	2.2	0.87	0.29	0
	25	2.5	0.49	2.2	0.54	0.21	0
	0	3.2	0.41	2.2	0.30	0.15	0

[a] SO_2 after 85% removal in SO_2 scrubbers.

[b] Particulate after 98% removal from boiler and 80% from dryer.

TABLE 23. ENERGY BALANCE[a]

Site	Power output (MW)	Input (Btux10^6/hr)	Coal energy (Btu/lb)	Dry refuse energy (Btu/lb)	Refuse moisture (%)	Coal/refuse mix (%)	Coal (ton/day)	Wet refuse (ton/day)
Traill, N. Dakota	21	224	6,590	7980	28	50/50	211	242
						75/25	311	119
						100/0	408	-
Marshall, Missouri	30	320	10,817	7980	40	50/50	189	426
						75/25	274	207
						100/0	355	-
Sibley, Iowa	2.5	26.7	10,377	8100	50	50/50	16.9	43.4
						75/25	24.2	20.7
						100/0	30.9	-

[a] Assume full capacity operation at 32% thermal efficiency for power generator. Dryer efficiency = 70%.

TABLE 24. ENERGY CONSUMPTION AND PARTICULATE EMISSION FOR DRYER[a]

Site	Coal/refuse mix (%)	Dryer energy (Btux10^6)	Particulate out (lb/day) After cyclone	Particulate out (lb/day) Before cyclone
Traill, N. Dakota	50/50	8.1	242	1210
	75/25	3.5	119	595
Marshall, Missouri	50/50	20.3	426	2130
	75/25	9.8	207	1035
Sibley, Iowa	50/50	2.6	43.4	217
	75/25	1.2	20.7	104

[a] Cyclone assumed to remove 80% of the particulates.

TABLE 25. MATERIAL BALANCE OUTPUT (tons/day)

Site	Coal/refuse mix (%)	SO_2 out	Ash out
Traill, N. Dakota	50/50		
	Coal	6.33	20.3
	Barley	0.174	2.83
	Wheat	0.220	4.73
	Sunflower	0	0.28
	Total	6.72	28.1
	75/25		
	Coal	9.33	29.9
	Barley	0.086	1.39
	Wheat	0.108	2.33
	Sunflower	0	0.0032
	Total	9.52	33.6
	100/0		
	Coal	12.2	39.2
Marshall, Missouri	50/50		
	Coal	13.2	19.8
	Wheat	0.298	6.41
	Corn	0.383	4.79
	Total	13.9	31.0
	75/25		
	Coal	19.2	28.8
	Wheat	0.145	3.12
	Corn	0.186	2.33
	Total	19.5	34.3
	100/0		
	Coal	24.9	37.3
Sibley, Iowa	50/50		
	Coal	1.18	1.77
	Corn	0.123	0.977
	Total	1.30	2.75
	75/25		
	Coal	1.69	2.54
	Corn	0.0373	0.466
	Total	1.73	3.01
	100/0		
	Coal	2.16	3.24

Land Disruption - Crop Residue

The major usage of land is for the storage of the crop waste. Since the crop residue is collected annually during a short period of time, provision is made for an entire year's volume. This analysis (Table 26) considers the residue to be stored in 30-ft-high open piles. A bulk density of 20 lb/ft^3 is assumed in the calculations. Actual practice may involve a feed preparation step (grinding/drying) at the time of harvest with storage in large silos. However, for purposes of estimating the maximum impact, the open piles are considered here.

TABLE 26. LAND USAGE FOR CROP RESIDUE

Site	Mixture coal/ residue (%)	Storage volume required (ft^3)	Land for 20-ft-high piles (acres)	Acres/ 10^9 Btu
Traill,	50/50	$8.8x10^6$	10	0.012
N. Dakota	75/25	$4.4x10^6$	5	0.011
Marshall,	50/50	$15.6x10^6$	17	0.013
Missouri	75/25	$7.8x10^6$	8	0.013
Sibley,	50/50	$1.6x10^6$	2	0.018
Iowa	75/25	$0.8x10^6$	1	0.019

SECTION 10

LARGE-SCALE COFIRING WITH COAL

COFIRING OF FORESTRY WASTES WITH COAL

Forestry wastes can be cofired with coal in large suspension-fired boilers. The wood must be finely divided and dry, but otherwise there is little difference between direct firing and cofiring. The sulfur emissions are reduced when the coal is mixed with wood in direct proportion to the average sulfur content in each feed. Total particulate emissions could be potentially much higher if proper control techniques are not employed. The grinding and drying operations of the wood are the largest contributors to the particulate emissions. NO_x emissions may actually be lower due to lower combustion temperatures, but more data are needed to support this conclusion. The CO emission is probably slightly higher for cofiring due primarily to the extra combustion required to dry the feedstocks.

COFIRING OF SUGARCANE FIELD WASTES WITH COAL IN LARGE UTILITY BOILERS

As with wood, it may be possible to fire sugarcane field waste (tops, leaves, etc.) with coal in large utility boilers. The feed must be finely divided and dried to be compatible with the coal in large suspension-fired boilers. The sulfur emissions in the cofiring of sugarcane waste are reduced in direct proportion to the average sulfur content of each feedstock. Both the particulate emissions and the carbon monoxide emissions are expected to be higher on a Btu output basis than for coal only. Drying and grinding (plus the combustion characteristics of the sugarcane waste) increases the potential particulate emissions. Drying, coupled with the lower Btu content of the sugarcane waste, also increases the carbon monoxide emission per 10^6 Btu of energy output. Estimates of NO_x emissions are difficult because of a lack of good data. Lower flame temperatures tend to produce less NO_x, but some researchers have estimated higher than expected NO_x from combustion of wood in similar wastes.[10] Because of the lack of good data, we are noting the deficiency in data and assuming no change in the NO_x emissions.

DATA

Table 27 summarizes the air emission data for the two cases considered and compares the data with the case of coal-only firing. A feed rate of 25% biomass residue and 75% coal is assumed. The location of the forestry residue case is Greene County, Alabama at the Greene Power Station of Alabama Power Company. The sugarcane residue case is based on a hypothetical coal-fired power plant to be constructed in Southern Florida in the future (as oil availability decreases). In both cases, Kentucky No. 6 coal is assumed, and the values of biomass collection, transportation, and feed preparation reported for direct firing of the forestry and sugarcane residue are incorporated in the data reported here. For simplicity, only the emissions per 10^6 Btu output are calculated rather than a complete material balance for any one specific case. This allows for calculation of any sized boiler or power plant. Very little data are available, especially regarding the NO_x emissions. The SO_x emissions are calculated directly from the average sulfur content of the feedstocks. The CO, hydrocarbon, and particulate data are taken from published USEPA data.[9]

TABLE 27. COMPARISON OF AIR EMISSION
(output, $lb/10^6$ Btu)

	Uncontrolled			Controlled			
	NO_x	SO_2[a]	Particulate	SO_2[b]	Particulate[c]	CO	HC
Coal, 100%	0.4 to 0.6	5.7	8.18	1.1	0.16	0.06	0.015
Coal, 75% Wood, 25%	1.0 to 1.2	4.3	10 to 14	0.86	0.3 to 0.4	0.14	0.10
Coal, 75% Sugarcane, 25%	0.6 to 0.7	4.3	7	0.86	0.2 to 0.4	0.27	0.15 to 0.17

[a] Based on 2.6% wt sulfur in coal

[b] 80% scrubber efficiency

[c] 98% control on combustion, 80% on dryer

SECTION 11

PYROLYSIS TECHNOLOGY

INTRODUCTION

In a study of this nature it is impossible to consider all, or even the majority, of the developing pyrolysis technologies. This overview presents a brief discussion of pyrolysis and describes the wide variety of possible reactor designs. This should allow the reader to place in proper perspective our analysis of the two processes selected (Purox® and Tech-Air).

Definitions

Before discussing pyrolysis, several definitions are in order. Pyrolysis is defined here as a process that thermally decomposes carbonaceous material in an atmosphere devoid of elemental oxygen. The products include gases, organic liquids, and a carbon char. Terms such as destructive distillation, thermal cracking, carbonization, and degasification have been used to describe pyrolysis. To be a true pyrolysis process, heat generation must occur in a vessel separate from the reactor, with indirect heat transfer through a wall, via a recirculating heat transfer media (sand, char, molten metal), or a hot flue gas produced by combustion of a fuel using a stoichiometric oxygen/fuel mixture. An important industrial example of pyrolysis is the coking of coal in batch feed retorts for metallurgical uses.

Gasification processes involve pyrolysis as well as reactions between the solid carbon char and gases such as CO_2 and H_2O. While a continuous flow pyrolysis reactor may contain a drying zone as well as a pyrolysis zone, a gasification reactor may also contain a char gasification zone (not necessarily as separate zones) and a char combustion zone. Gasification processes using combustion of char are autothermic in nature. The heat source may be internal to the reactor (char combustion) or the char may be combusted in a separate vessel with hot char or some other heat carrier recycled to the reactor. Oxygen (perhaps air) and steam may be injected into a gasification reactor; the reactions that occur are described in the following paragraph.

Reactions

The composition and relative amounts of products produced in the pyrolysis or gasification of solid wastes are extremely difficult to predict. The reactions that occur are simplistically described in Table 28. The temperatures at which various pyrolysis reactions occur may be roughly divided into three ranges:

TABLE 28. PYROLYSIS AND GASIFICATION REACTIONS

Pyrolysis of Solids and Condensible Gases (Organic Liquids)			
Carbonaceous solids	Heat	High and moderate molecular weight organic liquids (tars, oils, aromatics) + Carbon char + Low molecular weight organic liquids (some oxygenated) $+ CH_{4(g)} + H_2 + H_2O_{(g)} + CO + CO_2 + NH_3$ $+ H_2S + COS + HCN$	
Organic liquids	Heat	Aromatic organic liquids + Low molecular weight organic liquids + Gases + Char	
Pyrolysis Gas Phase Equilibria			
	$CH_4 + H_2O_{(g)}$	$\rightleftarrows CO + 3\ H_2$	Endothermic[a]
	$CO + H_2O_{(g)}$	$\rightleftarrows CO_2 + H_2$	Slightly exothermic
Char Gasification			
	$C + 2H_2O$	$\rightarrow CO_2 + 2H_2$	
	$C + H_2O_{(g)}$	$\rightarrow CO + H_2$	Endothermic[b]
	$C + CO_2$	$\rightarrow 2CO$	
	$C + 2H_2$	$\rightarrow CH_4$	Exothermic[c]
Char Combustion for Gasification Heat Source			
	$C + O_2$	$\rightarrow CO_2$	Exothermic

[a] Because of this reaction methane yield decreases greatly as temperature increases.

[b] High energy consuming reactions.

[c] At atmospheric pressure, the equilibrium conversion to methane is quite low and decreases as temperature rises from 1000°F to 1500°F. High pressure operation is required to achieve significant degree of hydrogenation of char or liquid products.

≤100°C	Drying (free water evolved)
200 to 500°C	Decomposition of high molecular weight compounds such as cellulose, lignin, proteins, and fats to relatively large quantities of organic liquids, some gases, and char
500 to 1200°C	Decomposition to permanent gases and char

The actual yield of products from carbonaceous solids is determined by the following factors: the characteristics of the input material (C/H/O ratios, type of organic structure, moisture content); the reaction conditions, such as heating rate (which is a function of particle size, heat transfer technique, temperature driving force); temperature levels; and residence time in various temperature zones of the reactor (which determines the extent of thermal cracking). Note that a pyrolysis process with concurrent solids flow may involve gasification of a significant quantity of char via reaction of water evolved from the drying zone of the reactor. In such a case, the moisture content of the feed may be a significant factor in determining char yield and gas yield.

Reactor Types

Only continuous flow reactors are considered in this discussion. To describe a process reactor adequately one must specify:

- Relative direction of gas and solids flow (cocurrent or countercurrent, also referred to as updraft or downdraft for systems with down-flowing solids)
- Method of heat transfer (direct or indirect)
- Method of solids removal (slagging vs. nonslagging)

The major reactor types now being developed or used for pyrolysis and gasification of solid wates include:

Vertical top feed shaft reactors
Vertical transport reactors
Multiple hearth reactors
Fluidized bed reactors
Rotary kiln reactors
Horizontal shaft reactors

By varying the relative direction of gas and solids flow, heat transfer methods and solids removal, over a dozen distinctly different processes are possible using the six types of reactors listed above.

Form of Energy Produced

Processes for pyrolysis or gasification of solid wastes may be selected and designed to produce varying amounts of organic liquids, char, and gaseous products. The products may be directly fired in a combustion chamber for steam production or processed for storage and subsequent use. Removing condensible organics and water vapor from gases can, however, produce a very significant water pollution problem. The higher the moisture content of the feed to the reactor, the larger is the volume of the wastewater. One of the processes to be evaluated in this study involved predrying, which is one method to minimize the problem.

PROCESSES

Tech-Air Process

The Tech-Air process, originally developed at Georgia Tech's Engineering Experiment Station, uses air to pyrolyze wastes in what might be described as a vertical kiln. The waste organic feed enters the top of the kiln and air is injected near the bottom to provide the partial combustion necessary to release the energy for pyrolysis. The products include: solid char (discharged from the bottom of the reactor); tars and liquids with varying boiling points and molecular weights; water; and noncondensible organic gases (hydrogen, carbon monoxide, carbon dioxide and nitrogen).

The Tech-Air process is used commercially to produce char and pyrolysis oils from wood waste. The gases in this case are burned to provide heat to dry the wood before it enters the kiln.

The process was also used to pyrolyze cotton gin waste in an early pilot scale unit at Georgia Tech. However, operating problems were encountered and, even though an extended run was achieved, the feed rates were lower than expected, and little or no condensible liquids were obtained. Other wastes were also run through the pilot scale unit but none of the other wastes are being considered in this study.

Purox® Process

The Purox® process differs from most other pyrolysis systems in three respects. First, and most important, oxygen is used instead of air (or indirect heating) to provide the partial combustion needed to supply the energy for pyrolysis. Second, all, or nearly all, of the organic matter is either oxidized or pyrolyzed into gaseous components (a medium Btu-content gas); no solid organic or char remains. Third, production of a liquid organic stream or oil is minimized or nearly eliminated; virtually the sole product is a medium Btu-content gas.

The large Purox® process pilot plant at South Charleston, West Virginia, has only been operated with municipal refuse as the feed. No experimental evidence is available that shows the Purox® process will function on the types of waste considered here. The Purox® converter appears to operate best when about 20% of the feed is noncombustibles. The noncombustibles form a melting bridge at the hearth zone, which tends to prevent unreacted organic materials from falling into the slag quench water below the hearth. Because of the low ash and negligible metals content of the waste feeds considered here, the converter configuration, particularly in and around the high-temperature hearth zone, would probably have to be altered to prevent excessive loss of organics into the slag pit. (Another alternative might be to mix the wood, cotton, or rice waste with municipal refuse to provide the higher metal content in the feed. That alternative has not been considered here.) SRI has assumed, and Union Carbide concurs, that the Purox® converter shape can be changed so it can accommodate the waste feeds being studied.

PROCESS FEEDS

Wood Residue

Wood residue that can be fed to pyrolysis units includes bark, sawdust, branches, other mill residue, and leaves or slash. With the exception of the leaves, these wastes have a higher moisture content -- sometimes as high as 70%, but more typically 50%. Ash content is low (1 to 3%) and the carbon-to-oxygen ratio is higher than in agricultural residues, due to the high lignin content of wood. Also, the residue is dense enough to make uniform in size for easy handling. Except for the high moisture content, the chemical and physical properties of wood make it easier to process in pyrolysis units than some of the other agricultural wastes.

The elemental analysis of the wood waste assumed for this study is as follows:

Element	Dry wt %
Carbon	49.6
Hydrogen	5.7
Oxygen	43.7
Nitrogen	0.2
All other	0.8

As with all natural materials, the analysis of the material actually being processed at any one time can vary over a sizeable range. For example, the carbon content on the limited number of samples of wood residue run by Georgia Tech ranged from 45 to 49%.

The feed is assumed to be 50% moisture.

An analysis of all other elements in the feed is provided by data[10,11] in Table 29.

Rice Hulls and Straw

Rice hulls and straw differ from wood waste in at least three important respects. First, they tend to contain much less water, as shown in Table 30 (wood waste contains typically 50% moisture; rice waste contains 5 to 10% moisture). Second, rice waste has a higher ash content, in some cases over 20% (see Table 30) whereas ash in wood typically runs 1 to 2%. Third, the

TABLE 29. APPROXIMATE ANALYSIS OF ALL OTHER COMPONENTS[a]

Cations	Percent of total feed	Anions	Percent of total feed
Iron	0.26	Chloride	0.14
Vanadium	0.09	Phosphate[b]	0.06
Manganese	0.14	Sulfur	0.005
Potassium[b]	0.06		
Zinc	0.035		
Copper	0.005		
Nickel	0.008		
Chromium	0.007		
Cobalt	0.002		

[a] Source: Reference 11.

[b] Source: Reference 12.

TABLE 30. ASSUMED ANALYSIS OF RICE HULLS AND STRAW

	Straw (wt %)	Hulls (wt %)
Carbon	38.5	35.8
Hydrogen	5.7	5.4
Oxygen	39.8	39.1
Nitrogen	0.5	0.6
Sulfur	-	0.1
Ash	15.5	19.0
Moisture	7.6	7.4

carbon-to-oxygen ratio in rice waste usually is less than 1, while the ratio is greater than 1 in wood waste. The lower ratio means that the heat of combustion is lower per pound of organic matter in rice waste than in wood. This lower heat, coupled with the low bulk density of rice waste and its tendency to agglomerate and bind rather than flow, may present operational problems in the pyrolysis units that are difficult to overcome.

As an indication of the variations in analysis that can be expected, the ash content of rice hulls has been reported as low as 13.6% and as high as 24.2%.

The waste rice hulls and rice straw available in California are:

Hulls	16,300 tons/yr
Straw	875,600 tons/yr

The feed to the Purox® system is assumed to be 8,000 tons/yr of hulls and 322,000 tons/yr of straw. So, the analysis of the rice waste feed to the Purox Unit is as follows:

Element	Wt %
Carbon	38.44
Hydrogen	5.69
Nitrogen	0.50
Oxygen	39.78
Ash	15.59
Moisture	7.60

The waste rice hulls and rice straws available in Mississippi are:

Hulls	9,000 tons
Straw	56,000 tons

While a 100-ton-per-day Tech-Air unit could be operated in Mississippi on rice waste alone, considerable cotton gin trash and cotton field waste are also available, so the assumed feed to a Tech-Air unit in Mississippi is a mixture of all these wastes. The analysis of that mixture is provided as part of the description of the cotton waste.

Cotton Waste

Cotton waste comes from ginning operations and from the field. The waste generally has the same composition. The elemental composition assumed for this waste is shown below:

Element	Dry wt %
Carbon	47.3
Hydrogen	6.0
Nitrogen	1.6
Oxygen	39.0
Ash	6.1
Moisture	5.0

Cotton waste is slightly different from other wastes being considered in that the moisture content is low and the carbon-to-oxygen ratio is high.

The mixed rice and cotton waste feed proposed for the Tech-Air process would come from Bolivar County, Mississippi. The quantities available are (in tons per year, dry wt.).

Cotton gin waste	12,000
Cotton field waste	32,000
Rice hulls	9,000
Rice straw	56,000
Total	109,000

The elemental composition of a feed composed of these wastes in the same proportions as generated -- which SRI has assumed for this mixed feed case -- would be as shown below:

Element	Dry wt (%)
Carbon	41.8
Hydrogen	5.8
Nitrogen	1.0
Oxygen	39.4
Ash	12.0
Total	100.0
Moisture content	6.5

Barley Straw Waste

Barley straw and rice straw have similar compositions except that the barley straw generally contains less inorganic matter, so the ash content is lower:

Element	Dry wt %
Carbon	43
Hydrogen	6
Nitrogen	0.5
Oxygen	45
Moisture content	7 to 10

About 185,000 tons a year of barley straw is available in Kern County, California as a feed to a pyrolysis unit. This quantity (560 tons/day) is too small to be feasible for operation of a Purox® process unit because the units come in 350-ton/day modules and a single module is seldom economic. However, another 110,000 tons of cotton field waste (80,000 tons per year) and cotton gin trash (30,000 tons per year) is also generated in Kern County. The combined waste would be sufficient to operate at least a 700-ton/day Purox® unit (two modules). Even this size operation is marginal, at best.

Assuming that the Purox® plant processes 700 tons/day of such waste 330 days/year and that the proportion of waste fed is the same as the proportions available, the estimated composition of the individual and mixed wastes are as shown on Table 31.

TECH-AIR WITH WOOD RESIDUE

Mass Balance

The Tech-Air unit would be designed to process 200 tons/day of wood waste containing 50% dry solids and 50% moisture, wastes such as bark, chips, sawdust, etc. This rate is equivalent to 16,700 lb of feed per hour

TABLE 31. ASSUMED ANALYSES OF BARLEY STRAW AND COTTON MIXED WASTE FEED (MOISTURE FREE BASIS)(WT %)

Element	Barley straw	Cotton gin and field waste	Barley/cotton mixed waste
Carbon	43	47.3	44.6
Hydrogen	6	6.0	6.0
Nitrogen	0.5	1.6	0.9
Oxygen	45.0	39.0	42.8
Ash	5.5	6.1	5.7
Total	100	100	100
Moisture	10	5	7.5

(the hour of operation being the basis of mass and energy balances provided in this section). The basic components of the feed are cellulose and lignin. The elemental analysis of the dry solids is approximately as follows:

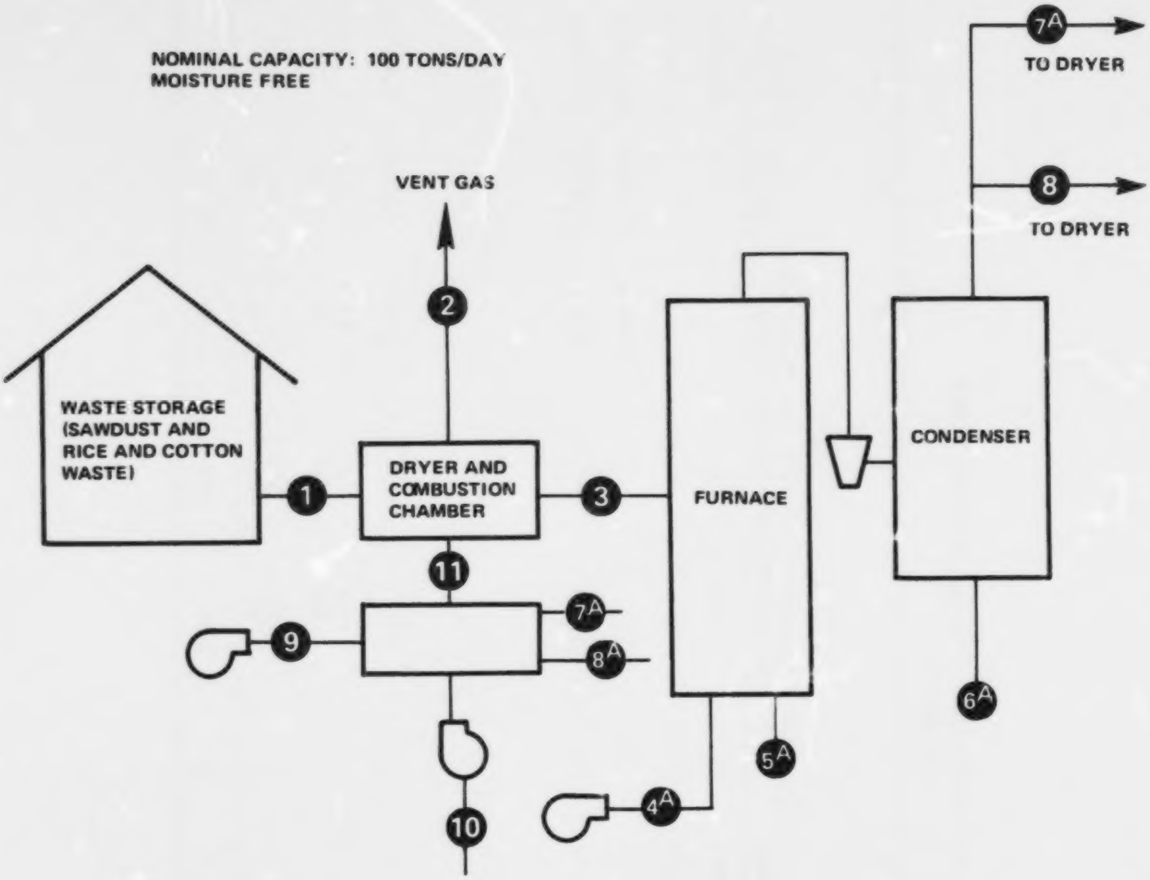
Element	Wt %
Carbon	49.6
Oxygen	43.7
Hydrogen	5.7
Nitrogen	0.2
All other	0.8
	100.0

The above elemental analysis was used in SRI calculations. Some variations in the percentages shown above are common and expected.

The flowsheet for the Tech-Air process using wood residue feed is shown in Figure 19. The weights of the major elements of each numbered flow on Figure 19 are provided in Table 32.

To derive the stream flows in Table 32, SRI made a number of assumptions required primarily because the data available in Georgia Tech's report[10] did not specifically provide the information needed to develop the case considered.

The major piece of missing data was the quantity, composition, and heat content of the flowstream SRI has chosen to call the tars or condensible pyrolysis gas. SRI has assumed that such a stream or streams exist because of the "carbon" lost in each run. Such carbon losses ranged from 2 lb/100 lb of feed up to nearly 14 lb/100 lb of feed. Since the carbon loss cannot very well be built up in the pyrolysis furnace, one must assume that either carbon or organic materials are escaping without being accounted for.



NOMINAL CAPACITY: 100 TONS/DAY
MOISTURE FREE
VENT GAS
2
WASTE STORAGE (SAWDUST AND RICE AND COTTON WASTE)
1
DRYER AND COMBUSTION CHAMBER
3
11
9
7A
8A
10
FURNACE
4A
5A
CONDENSER
6A
7A
TO DRYER
8
TO DRYER

Figure 19. Georgia Tech pyrolysis process.

Using the ultimate analyses provided for Run 15, it was possible to devise a complete energy balance and the material balance for the Tech-Air system. The latter is as recorded on Table 32. That material balance also includes a mass balance for carbon, hydrogen, oxygen, and nitrogen.

To close the material balance, the following material must be accounted for: 6.3 lb of carbon, 0.7 lb of hydrogen and 8.4 lb of oxygen per 100 lb of dry feed. This material, if available (and SRI has assumed it is) can provide sufficient extra energy when combined with the combustible gases used for drying the feed to permit operation of the pyrolysis furnace with about 0.2 to 0.3 lb of air per pound of feed rather than the 0.5 lb of air per pound of feed that would be needed otherwise. (SRI used 0.22 lb of air per pound of feed, although this may be a slightly lower ratio than what can actually be used.) The advantage of the lower air-to-feed ratio is that a higher proportion of the feed becomes saleable fuel oil or char.

TABLE 32. TECH-AIR PYROLYSIS PROCESS STREAM FLOWS (lb/hr)

Stream	1	2	3	4	5	6	7	8	9	10	11
	Wet sawdust	Drier vent gas	Dried sawdust	Pyrolysis air	Char	Oil - associated H_2O	Non-condensible pyrolysis gas product	Tars or condensible pyrolysis gas product	Combustion air	Mix-air	Gas to drier
Carbon	4132	1,291.1	4132		1876	964.0	763.8	528.2			1,291.9
Hydrogen	473	1,363.6	473		104	80.8	76.0	61.6			486.5
Nitrogen	18	103,279.8	18	1394	11	2.0	1400		9883.6	91,996.2	103,279.8
Oxygen	3647	42,415.5	3647	424	663	367.2	1128.5	704.3	2985.7	27,790.0	35,398.6
Sulfur	1										
Ash	63		63		103						
Other											
H_2O	8333	12,272.5	439	18	-		700	1112.6	128.7	1,197.7	4,437.5
		(877.1) (H)	370.2 (O)	16 (O)			77.8 (H)	989 (O)	14.3 (H)	133.1 (H)	
		7016.9 (O)	48.8 (H)	2 (H)			622.2 (O)	123.6 (H)	114.4 (O)	1064.6 (O)	
Total	16,667	148,350.8	8772	1833	2757	1414	4068.3	2406.4	12,998	120,983.9	

The hourly flow of the minor elements in the feed and char as reported by Georgia Tech (Run 15) are as follows:

	Feed (lb)	Char (lb)
Iron	22	55
Manganese	12	13
Vanadium	7	11
Potassium	5	-
Zinc	3	12
Nickel	1	3
Chromium	<1	<1
Copper	<1	<1
Cobalt	<1	<1
Chloride	12	3
Phosphate	5	-
Sulfur	<1	<1

With the possible exception of the chloride ion, all of the minor elements appear to remain in the char. Even if the chlorides are all volatilized, their concentration in the offgases would be very low (10 lb/hr or 67 ppm by weight in the dryer vent gas).

The major products of pyrolysis, in pounds per hour, are:

Char	2757
Oil	1414
Gas (both tar or condensible and noncondensible)	4662
Water	1813

SRI has assumed that by proper design and operation the water, part of which might report in the oil fraction, could all end up as part of the pyrolysis gases used to provide heat for drying the wet wood residue.

The water shown separately above would be an integral part of the offgases, unless it were impossible to keep it out of the oil fraction. In either case, the quantity of water shown, 1813 lb, came from:

Moisture in the feed and pyrolysis air	457
Product of pyrolysis reactions	1356
Total	1813 lb

The water formed by the pyrolysis reaction was determined by assuming a reasonable C/H/O ratio for the organic component in both the oil fraction and the tar or noncondensible gas fraction. With the above assumption and the elemental analysis, the percent of water in each fraction was calculated.

The above method of calculation is a departure from the method used by Georgia Tech.[11] (They assumed that all the oxygen in the oil/water mixture was in the water and they ignored the missing hydrogen and oxygen, along with the "lost" carbon. This, again, was on the assumption that the missing hydrogen and oxygen had combined to form water, even though the ratios of the missing hydrogen and oxygen indicate otherwise.) The oily products of pyrolysis of wood are known to be oxygenated organics. Such oils typically contain 35 wt % oxygen.

Using the SRI procedure for calculating the water has three effects on the analysis: it increases the quantity of oil formed; it decreases the unit heat content of the oil product; and it changes the energy balances of the system, particularly those in and about the pyrolysis furnace.

According to SRI's method of calculation, 1414 lb of oil product are formed per hour, with a heat of combustion of 11,806 Btu/lb. Using the Georgia Tech procedure, 1008 lb of oil are produced, with a heat of combustion of 16,300 Btu/lb.

The effect on energy balance of the alternative methods of calculation is described in the next subsection (Energy Balance).

The stream unaccounted for in the Georgia Tech analysis[11] has been assumed by SRI to be added as part of the fuel for drying the wood prior to pyrolysis. The analysis of that fuel is shown on Table 33.

As is shown by the energy balance, this fuel provides more than enough heat on combustion to dry the wood from 50% moisture to 5% moisture or less.

TABLE 33. FUEL FOR WOOD DRYING

Component	Lb	Wt %
$CH_{14}O$[a]	1294	20.0
CO	825	12.7
H_2	29	0.4
CH_4	119	1.8
C_2	58	0.9
C_3	24	0.4
C_4	10	0.2
CO_2	903	14.0
N_2	1400	21.6
H_2O	1813	28.0
Total	6475	100.0

[a] Tar or condensible gas

Energy Balance

The energy balances in the system are important, not only to indicate what percent of the energy in the original feed becomes available in the products but to indicate the operability of various system units, such as the pyrolysis furnace and the feed dryer.

The heats of combustion of the dried feed and char were measured with a Parr bomb at 7968 and 11078 Btu/lb, respectively. The heats of combustion of the noncondensible gases can be calculated and the heat of combustion of the oil and condensible gas can be estimated from their molecular composition.

The overall energy balance in millions of Btu per hour of operation is as follows:

	Heat of combustion	Lb/hr	10^6 Btu/hr In	10^6 Btu/hr Out
Feed	7968	8630[a]	68.76	
Char	11078	2757		30.27
Oil	11806[b]	1414		16.67
Totals			58.76	46.94

---

[a] The 7968 Btu heat of combustion was presumably determined on a feed that contained 3.44% moisture:

$$\frac{8333}{0.9656} = 8630 \text{ lb}$$

[b] Calculated value.

Over 68% of the original energy is recovered as usable energy in the two products. The energy consumed, 21.82 million Btu/hr, must be sufficient to perform the pyrolysis and drying.

The pyrolysis reaction can be depicted by the following equation:

$$C_{17.217}H_{23.66}O_{11.40(S)} + 0.66\ O_2 = C_{7.817}H_{5.20}O_{2.072(S)} +$$

$$C_{402}H_{404}O_{115(\ell)} + C_{2.20}H_{3.80}O_{2.20(g)} + 1.47\ CO + 1.03\ CO_2 +$$

$$0.72\ H_2 + 0.37\ CH_4 + 0.10\ C_2H_6 + 0.03\ C_3H_8 + 0.01\ C_4H_{10} + 3.77\ H_2O$$

The enthalpy ΔH of this reaction is an estimated -129.503 Kcal/g-mol, which would provide 4.65 million BTU/hr of energy to the pyrolysis system. Put another way, the energy balance around the pyrolysis furnace based on this reaction is as follows, in millions of Btu/hr:

	Heat of combustion	Lb/hr	10^6 Btu/hr In	 Out
Feed	7,968	8,630	68.76	
Char	11,078	2,757		30.27
Oil	11,790	1,414		16.67
Noncondensible gases				10.17
Tars or condensible gases				7.00
Totals			68.76	64.11

The difference between the energy in and out is 4.65 million Btu.

If all 4.65 million Btu are used to heat the pyrolysis products, they would leave the pyrolysis furnace at about 1050°F. Even though this estimate does not include any heat losses from the furnace itself, it indicates that the air-to-feed ratio used is quite adequate to provide stable operation of the furnace.

The sensible heat in the condensible and noncondensible gases, plus the energy from their combustion (assuming the gases from the condensor enter the combustion chamber at about 200°F), would provide the following energy for drying the wet wood, in millions of Btu/hr.

	10^6 Btu/hr
Heat of combustion	
Noncondensible gases	10.17
Tars or condensible gases	7.00
Sensible heat	0.45
Total	17.62

There are 7895 lb of water to be removed from the residue feed in the dryer. The energy available is 2232 Btu/lb of water to be removed. Most commercial dryers reduce the moisture in the wood to 5% or less with 1700 to 1800 Btu/lb of water. The energy available for drying is also more than adequate for the purpose.

Energy is also consumed in the process for:

- Loading the refuse into the system via fork lift or front-end loader

- Conveyors, pumps, lifts, fans, etc., that are part of the process equipment.

The loading operation (17,000 lb/hr) assuming a Hyster Model 50 that consumes 2.5 gal/hr for operation would require 0.31×10^6 Btu/hr.

The process energy could be supplied by a 100 kW power substation or a self-contained 100 kW motor-generator burning 19 gal of diesel oil per hour (140,000 Btu gal). The 200 kW requirement is based on the design in the RM Parsons's report rather than using the 150 kW capacity originally suggested by Tech-Air.

Overall, the process energy requirement is:

	10^6 Btu/hr
Loading	0.30
Processing	1.95 to 2.66
	3×10^6

and the net energy available from the system is 47.2 - 3, or 44.2 million Btu/hr or $44.2\times10^6/16,667 = 2,650$ Btu/lb of wet feed.

Pollution and Hazards

The Tech-Air system using wood residue as feed is unique in that no solid or liquid residue results. Little or no pesticide is used on the woods under consideration (Humboldt County, California) so pesticide residue is probably not significant.

Land Disruption--

Land use is minimal. An acre appears more than adequate for feed and product storage and for siting of the three trailers that would hold the process equipment. If the plant operates 300 days/yr (assuming 2 moves/year) and provides char and oil with a net combined energy content of 318×10^9 Btu/yr (24 hr/day, 300 days/yr, 44.2 million Btu/hr), the land requirements are 0.003 acre/10^9 Btu/yr.

Air Pollution--

There are three sources of air emissions from the process:

- Loader
- Motor-generator (if used)
- Offgases from the wood residue dryer

Measured emissions from similar diesel engines installed in the loader and motor-generator are shown in Table 34.

TABLE 34. DIESEL ENGINE EMISSIONS
(grams per brake horsepower-hour)

	Hydrocarbons + NO_x	Carbon monoxide	Smoke
Motor-generator (280 hp) Brake horsepower 160	11	5	<3%
Loader 68 hp Brake horsepower 50	11	5	-3%

Table 35 provides the results of a stack emission test of the dryer offgases. Based on these results, the emissions from the total system are as follows (in pounds per hour):

	Dryer	Engines	Total
Carbon monoxide	4.5	2.3	6.8
NO_x[a]	negl.	5.1	5.1
Particulates	0.06	negl.	0.06

[a] Includes some hydrocarbons.

All other possible pollutants -- such as ammonia, sulfur dioxide, hydrogen sulfide -- are considered present in negligible amounts.

The summary of known impacts is provided on Table 36. The process also could generate some unquantifiable pollutants. The most likely are particulates (fugitive dust) from the handling of the residue and its grinding prior to being fed to the pyrolysis furnace. Careful handling and hooding are needed to keep this source from adding significantly to the pollution levels. Improper handling of the char product could also generate fugitive dust.

Overall, this process should be an extremely clean source of energy.

TABLE 35. ANALYSIS OF DRYER STACK EFFLUENTS

A. COMPONENTS DETECTED

Component	Composition by volume	Test method	Mass rate of pollutants (lb/min)
Water	14%	Liquid impinger collection	N/A[g]
Oxygen	9.0%	GCTC[a]	N/A
Nitrogen	69%	GCTC	N/A
Carbon dioxide	7.7%	GCTC	N/A
Carbon monoxide	30 ppm	MSA[b]	6.5×10^{-2}
Particulates	14 micro gms/ft^3	Liquid impinger collection	9×10^{-4}

B. COMPONENTS TESTED FOR BUT NOT DETECTED

Component	Threshold sensitivity of tests[f] (ppm)	Test method
Hydrogen	0.0009	GCTC
Methane	0.0009	GCFID[c]
Sulfur dioxide	0.4	MSA[d]
Nitrogen dioxide	0.04	MSA[e]
Ammonia	0.09	Odor
Hydrogen sulfide	0.009	Odor

[a] Gas chromatography -- thermal conductivity detector

[b] MSA -- Mine Safety Appliance Co. Test Part No. 91229

[c] Gas chromatography -- flame ionization detector

[d] MSA -- Mine Safety Appliance Co. Test Part No. 92623

[e] MSA -- Mine Safety Appliance Co. Test Part No. 83099

[f] These components would have to be present in concentration shown to be detected; therefore, these results represent the maximum amounts of these components which could be in the stack gas

[g] N/A -- not applicable

Source: Reference 11.

TABLE 36. ENVIRONMENTAL IMPACTS OF TECH-AIR PYROLYSIS
OF WOOD RESIDUE

Impact		Resource extraction	Onsite processing or storage	Transport to conversion plant	Conversion plant
Land disruption and use	Acres/ 10^9 Btu/ yr/output				0.003
Water pollution					
Input	(gal/10^6 Btu)				0.57
Output	(gal/10^6 Btu)				0
Waste heat	(Btu/10^6 Btu)				0
Ammonia	(lb/10^6 Btu)				
Phosphorus	(lb/10^6 Btu)				0
Salts	(lb/10^6 Btu)				0
Metals	(lb/10^6 Btu)				0
Pesticides	(lb/10^6 Btu)				0
Air pollution					
NO_x	(lb/10^6 Btu)				0.12
CO	(lb/10^6 Btu)				0.15
SO_x	(lb/10^6 Btu)				negl.
H_2S	(lb/10^6 Btu)				negl.
Particulates	(lb/10^6 Btu)				negl.
Pesticides	(lb/10^6 Btu)				0
Hydrocarbons	(lb/10^6 Btu)				incl. in NO_x
Organisms	?				0
Solid waste total	(lb/10^6 Btu)				0

Hazardous Materials--

The products of pyrolysis are extremely diverse. See Tables 37 and 38 for lists of likely products.

TABLE 37. COMPOUNDS FORMED BY WOOD CARBONIZATION[a]

Carbon dioxide
Ammonia
Water
Formaldehyde
Formic acid
Methanol
Methylamine
Glyoxal
Acetaldehyde
Acetic acid

[a] Source: Reference 13.

TABLE 37 (continued)

Methyl formate
Glycolaldehyde
Glycolic acid
Ethyl alcohol
Dimethylamine
Acrylic acid
Acetone
Allyl alcohol
Propionaldehyde
Methyl acetate
Propionic acid
Isopropyl alcohol
Propyl alcohol
Methylal
Trimethylamine
Succinic anhydride
Furan
Crotonaldehyde
Biacetyl
3-Butenoic acid
Butyrolactone
Crotonic acid
Methacrylic acid
Methacrylic acid, polymer
2-Butanone
2-Buten-1-ol
Butyric acid
Isobutyric acid
Methyl propionate
Isobutyl alcohol
2-Furyl methyl ketone
Catechol
5-(Hydroxymethyl)-2-furfuraldehyde
4-Methyl 2-furoic acid
Methyl 2-furoate
Maltol
Pyrocinchonic anhydride
Pyrogallol
2-Picolene
2-Methyl-2-cyclopenten-1-one
4-Methyl-2-cyclopenten-1-one
2,5-Dimethylfuran
1-(3 or 4) Cyclohexanedione
2-Hydroxy-3-Methyl-2-cyclopenten-1-one
-Methyl- -ethylacrolein
Cyclohexanone
3-Hexen-2-one
Mesityl oxide
1-Hydroxy-2-butanone acetate
2,3-Hexanedione
4-Methyl-2-pentenoic acid
Hydroxy-2-propanone propionate
Levoglucosan
Cyclohexanol
Tetrahydro-2-5-dimethylfuran
3-Hexanone
Butyl methyl ketone
2-Methyl-3-pentanone
Caproic acid
Isocaproic acid
-Methylvaleric acid
Methyl valerate
Toluene
o-Cresol
m-Cresol
p-Cresol
Guaiacol
1-Methoxy-2,3-dihydroxybenzene
5-Methyl pyrogallol
Lutidine
1-Methyl-2-cyclohexen-5-one
Propylfuran
2,3,5-Trimethylfuran
1-Heptyne
Cyclohexanecarboxaldehyde
Dimethylcyclopentanone
2-Ethyl-2,3-dihydro-5-methylfuran
5-Heptenoic acid
Butyrone
Enanthaldehyde
Methyl caproate
Enanthic acid
Heptane
Benzofuran
m-Xylene
o-Ethylphenol
2,3-Xylenol
2,4-Xylenol
3,5-Xylenol
Creosol
6-Methylguaiacol
2,6-Dimethoxyphenol
Methoxy-4-homocatechol
2,4-Dimethyl-4-cyclohexene-1-one
Methylcyclopentanone
3-Isopropyl-2-cyclopenten-1-one

TABLE 37 (continued)

Trimethylcyclopentanone
3,5-Octanedione
Caprylic acid
Methyl enanthate
Dihydroxycaprylic acid
4-Vinylguaiacol
Cumene
Pseudocumene
3,5-Dimethylguaiacol
4-Ethylguaiacol
Homoveratrole
2,6-Dimethyoxy-4-Methylphenol
5-Propylpyrogallol
Isophorone
Amylfuran
2,4,4-Trimethylcyclohexanone
Cyclohexanepropionaldehyde
3,3,5-Trimethylcyclopentanone
Pelargonic acid
Naphthalene
Estragole
Eugenol
Isoeugenol
Cymene
Durene
Thymol
4-Propylguaiacol
2,6-Dimethoxy-4-ethylphenol
A5-propyl-monomethyl ether of pyrogallol
Camphene
Limonene
Nopinene
Pinene
Sylvestrene
-Terpinene
Terpinolene
Camphor
Borneol
Cineole
Melene
Frenchyl alcohol
Isofrenchyl alcohol
-Terpineol
Capric acid
1,3,3-Trimethylbicyclo(2.2.2) 5-octen-2-one
5-Propyl-1,3-dimethoxy-2-hydroxybenzene
2,5-Difurfuryledine-1-cyclopentanone
Cadinene
Pentadecane
Palmitic acid
Heptadecane
Chrysene
Retene
Oleic acid
Stearic acid
Octadecane
Nonadecane
Abietic acid
Pimaric acid
Arachidic acid
Eicosane
Heneicosane
Behenic acid
Docosane
Tricosane
Lignoceric acid

TABLE 38. COMPOUNDS REPORTED TO BE PRESENT IN HARDWOOD SMOKE[a]

Acids

- Formic
- Acetic
- Propionic
- Butyric
- Aconitic ?
- Tricarballylic ?
- α-Ketoglutaric ?

Alcohols

- Methanol
- Ethanol

Carbonyls

- Formaldehyde
- Acetaldehyde
- Acetone
- Diacetyl
- Furfural
- Methyl Furfural

Hydrocarbons

- 3,4-Benzpyrene
- 1,2,5,6-Dibenzanthracene
- 20-Methylcholanthrene

Phenols

- Cresols
- Creosol
- Guaiacol
- Guaiacol derivatives
  - 4-Ethyl
  - 4-Propyl
  - 6-Methyl
  - 6-Ethyl
  - 6-Propyl
- Pyrogallol ethers
  - 1-O-Methyl
  - 1,3-Dimethyl
- 1,3-Dimethyl Pyrogallol derivatives
  - 5-Methyl
  - 5-Ethyl
  - 5-Propyl
- 1-O-Methyl-5-Methyl Pyrogallol
- Veratrole
- Xylenols

Others

- Ammonia
- Carbon dioxide
- Resins
- Water
- Waxes

---

[a] Source: Reference 13.

SRI's Chemical Environmental Group has identified (from the chemicals listed in Table 37) 22 chemicals or chemical groups that are or might be carcinogens or otherwise hazardous materials. These chemicals and the reasons they are considered hazardous are listed below:

• Dimethylamine	May form the potent carcinogen, dimethylnitiosamine, under conditions of nitrosation.
• Butyrolactone	Structurally related to the known carcinogen, beta-propiolactone. However, as a five-membered lactone, butyrolactone is expected to be less reactive as an alkylating agent and hence less carcinogenic. No carcinogenic effects have been observed in tests on mice by oral, topical, or subintaneous

	administration and in rats by subintraneous administration. Tumors were produced in a single test in weanling rats by oral administration but the significance of these results is questionable due to inadequate protocol.
• Catechol	Known to be a cocarcinogen due to its ability to significantly enhance the carcinogenicity of benzo[a]pyrene in mouse skin.
• Pyrogallol	Known to be a cocarcinogen due to its ability to enhance the carcinogenicity of benzo[a]pyrene in mouse skin.
• O-Cresol • M-Cresol • P-Cresol	Known to be tumor promoters because of their ability to elicit skin tumors in mice by repeated applications following a single, subcarcinogenic dose of 7,12-dimethylbenz[a]anthracene.
• Estragole	Should be considered a suspected carcinogen until proven otherwise by adequate testing because of its structural relationship to safrole, a known carcinogen in mice and rats.
• Limonene	Known to have tumor promoting activity in mouse skin.
• Pinene	Reported to have tumor-promoting activity in mouse skin.
• Chrysene	Has produced skin tumors in mice following repeated topical applications. Produced low incidence of local sarcomas in mice following subcutaneous administration. Is an initiator of skin tumors in mice when followed by promotion with croton oil. Hence, chrysene should be considered a weak carcinogen.
• Oleic acid	Reported to have tumor-promoting activity in mouse skin.

• Octadecane	Known to be a cocarcinogen in mice by its activity to enhance the rate of induction of skin tumors by benzo[a]pyrene. It is also a known tumor-promoter in mice by its ability to elicit skin tumors by repeated topical applications following a single, subcarcinogenic dose of 7,12 dimethylbenz[a]anthracene.
• Eicosane	Same as for Octadecane.
• 3,4 Benzpyrene	Is both a local and systemic carcinogen in all animals in which it has been tested by several routes of administration including oral, topical, intratracheal and inhalational, and subcutaneous.
• 1,2,5,6 Dibenzanthracene	A local and systemic carcinogen in mice, rats, guinea pigs, frogs, pigeons, and chickens by different routes of administration including oral, topical, and subcutaneous.
• 20-Methylcholanthrene	A local and systemic carcinogen in several species, including mice and rats, by several routes of administration including topical, subcutaneous, intratracheal, and oral.
• Cresols	As cited previously (Table 37) cresols are known tumor promoters.
• Creosol	One of the active constituents of creosote. Wood creosote is a wood tar phenol mixture which is an irritant and probable tumor-promoter. Coal tar creosote is an aromatic hydrocarbon containing coal tar distillate which is carcinogenic in animals by topical application.
• Xylenols	As cited above (Table 37) xylenols are known tumor-promoters.

With this information in hand, we must consider the pyrolysis oil a possible carcinogen and recommend that it be handled as such until data are available on the pyrolysis oil itself. The carcinogenic nature of several of the components of the pyrolysis products should prompt a study of the various streams and emission from the plant to determine the extent of the hazard.

PUROX® WITH WOOD RESIDUE

Refuse, the only waste fed so far to the large pilot plant, not only has a higher percentage of noncombustible (metal, glass, dirt) material, but generally has a lower moisture content than undried wood waste. The major effect of changing from refuse to wood, other than the converter configuration changes already mentioned, is the higher oxygen-to-feed ratio required. The extra oxygen is needed to increase the heat release in the converter in order to evaporate the extra water present in the wood. (Less energy is needed to melt the smaller amounts of inorganic residue in the wood, but this is more than offset by the heat needed for the moisture evaporation).

The proposed location to process wood residue by the Purox® system is somewhere in Humboldt County, California. The county is small enough and the quantities of avilable wood residue large enough that the plant can probably be located near lumber mills; no further purification, drying, or major compression of the product gas would be necessary to prepare it for pumping to plants that can use it.

Mass Balance

Purox® converters are designed to process 350 tons/day of refuse. For wood residue, a system is envisioned with three converters that would process 83,333 lb/hr (1000 tons/day) of wood waste.

The flowsheet for the Purox® process using wood residue feed is provided as Figure 20.

An examination of the elemental and basic composition of the wood residue and refuse (Table 39) shows the big difference between the moisture and ash content in the two feeds. However, the sum of moisture plus ash in wood, 50.4%, and in refuse, 45.0%, is not that different. Also, the carbon-to-hydrogen ratio (and even the carbon-to-oxygen ratio) is about the same. Based on this similarity, one can assume that the distribution of pyrolysis products is about the same for wood residue as for refuse.

Table 40 shows the estimated analysis of the offgas before and after it has passed through the condenser to remove most of the water and the condensible organics.

Union Carbide, the developer of the Purox® process, has found that more oxygen is needed (0.23 lb/lb feed) to achieve the offgas composition shown on Table 40 than is necessary for refuse (0.2 lb/lb refuse). The oxygen-to-feed ratio for wood residue was determined from an analysis of the energy release and the energy requirements in the case of refuse feed as compared to the case of wood residue feed.

The ratio actually required may be somehwat lower than the 0.23 indicated. The actual ratio used will be set so the temperature of the gases leaving the converter will require some cooling (adiabatic) in the spray condenser. SRI has assumed that the gases leaving the converter must have

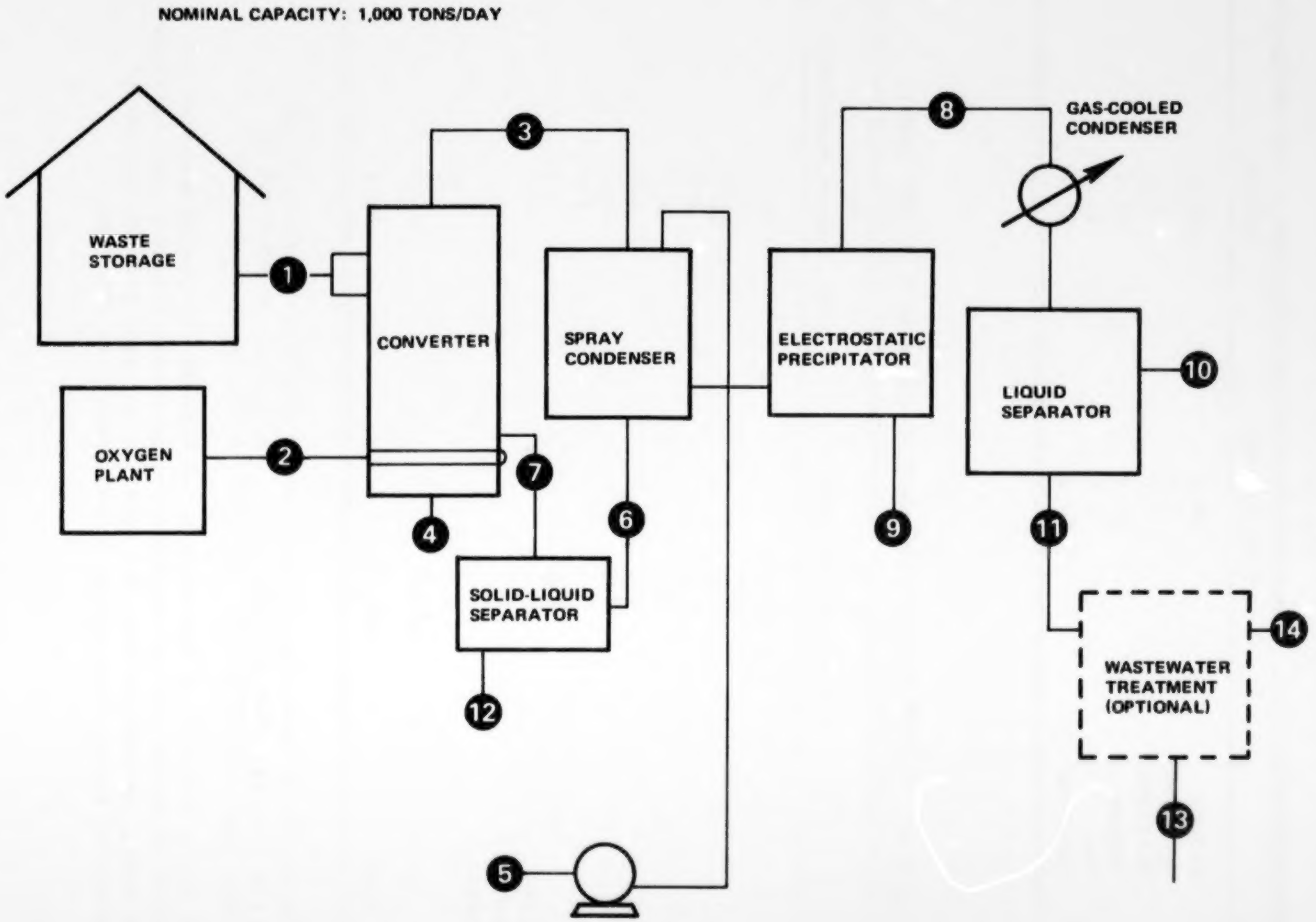


Figure 20. Purox® process.

TABLE 39. COMPARISON OF WOOD RESIDUE AND REFUSE COMPOSITION (wt %)

	Wood residue	Refuse
Carbon	24.8	29.0
Hydrogen	2.8	3.2
Nitrogen	0.1	N/A
Oxygen	21.9	22.8
Ash	0.4	17.9
Moisture	50.0	27.1

TABLE 40. PUROX® PRODUCT GAS ANALYSIS (FROM WOOD RESIDUE FEED)

	Wt % (wet product gas)	Vol % (cool, noncondensibles)
CO	20.9	40.5
CO_2	24.4	30.1
H_2	0.7	18.8
CH_4	1.3	4.4
C_2H_2	0.2	0.5
C_2H_4	0.8	1.6
C_2H_6	0.1	0.2
C_3	0.4	0.4
C_4+	1.5	1.2
$(COH_2)N$	0.1	0.2
Condensible organic	1.6	--
N_2	0.5	1.0
H_2O	47.5	1.0
TOTAL	100.0	99.9

2 million Btu/hr of heat removed in order to condition it for passage through the electrostatic precipitator. The cooling is achieved by evaporating just over 2000 lb/hr of water in the spray condenser.

The extra oxygen used was distributed between the carbon monoxide and carbon dioxide to use the carbon remaining after distributing the available hydrogen among the hydrocarbons and water in the same proportions as it was distributed among these products when refuse was the feed.

Union Carbide has considered the ultimate fate of all other components because these and many more minor elements are likely to be present in the refuse. From their analyses of the slag and metal residue fractions and the material condensed from the offgases, all other components are found entirely in the slag residue with the following exceptions: chromium, copper, manganese, nickel, zinc, sulfur, and chlorides.

Based on Union Carbide's analyses, the fate of the minor elements in the wood residue is as shown in Table 41.

TABLE 41. DISPOSITION OF MINOR CONSTITUENTS IN WOOD RESIDUE FED TO PUROX® PROCESS (lb/hr)

	Feed	Slag (or metal)	Wastewater	Offgas
Iron	108	108	N.D.[a]	
Manganese	58	58	0.08	
Vanadium	38	38	--	
Potassium	25	N.D.	N.D.	
Zinc	15	14	1.2	
Nickel	3	3	0.03	
Chromium	3	3	0.001	
Copper	2		<0.0001	
Cobalt	<1	<1		
Chloride	58	N.D.	58	
Phosphate	25	25	N.D.	
Sulfur	2			2

[a] N.D. = no data

Energy Balance

The energy balance about the converter in millions of Btu/hr of operation is as follows:

	lb/hr	Btu/lb	10^6 Btu/hr In	10^6 Btu/hr Out
Feed	83,333	4126[a]	343.83	
Gas				235.02
Organic in wastewater				17.46
TOTAL			343.83	252.48

---

[a] The heat of combustion (7968 Btu/lb) was calculated for a feed that contained 3.44% moisture. A feed with 50% moisture should have the heat of combustion shown.

Thus, 68% of the energy available in the feed, as measured by the heat of combustion, is still available in the fuel gas product. The 91.35 million Btu/hr consumed by the process (343.83 - 252.48) is used to perform the pyrolysis which, in this case, includes drying the feed. The reaction involved in providing the energy for pyrolysis and drying can be described as follows:

$$\begin{aligned} C_{17.22}H_{23.65}O_{11.40} + 5.99O_2 = {} & 7.66\,CO + 5.69\,CO_2 + 7.12H_2 + 3.93H_2O \\ & + 0.83CH_4 + 0.10C_2H_2 + 0.30C_2H_4 + 0.04C_2H_6 \\ & + 0.08C_3 + 0.226\,C_4 + 0.03COH_2 + 0.37C_2H_4O(1) \end{aligned}$$

The theoretical heat of the reaction (ΔH reactions -518.6 Kcal/g-mol) would provide 93.35 million Btu/hr of energy, which is in fair agreement with the 91.35 million Btu/hr, considering the number of assumptions required to derive the figure.

Much of the 91.35 to 93.35 million Btu/hr is present in the gases leaving the converter. If the gases leave the converter at 250°F, their sensible heat content would be 56.99 10^6 Btu/hr, as shown in the following tabulation:

	lb/hr	H_{77}^{250} Btu/lb	Sensible heat 10^6 Btu/hr
H_2O	48,733.9	1,118.9	54.53
Other gases	52,268.2	41.5	2.17
Liquifier Organic	1,640.9	175	0.29
TOTAL	102,643		56.99

Some additional heat would leave the converter in the hot slag. If we assume the slag temperature is 2777°F, the sensible heat in the slag would be 0.17 million Btu -- (2777 - 77)[*](0.2)[†](315)[‡].

The heat loss in the converter then is around 34 to 36 10^6 Btu/hr. This loss appears about the same as the heat loss when the feed is refuse instead of moist wood.

---

[*] Temperature difference, °F

[†] Specific heat of solid, Btu/lb

[‡] Weight of slag, lb

Energy is also consumed in the processing of wood residue to:

- Operate the air separation plant
- Load the waste into the system
- Drive the various motors and fans required in the process itself

The air separation plant requires an estimated 300 kWh. If we assume that 9400 Btu of fuel energy makes 1 kWh of electricity, the energy requirement for air separation is 28.2 million Btu/hr.

The loading operation (83,330 lb/hr), assuming two 120-hp loaders that each consume 6 gal/hr of diesel fuel, requires 1.5 million Btu hr.

No definite value was found for the amount of energy required to drive the converter and gas cleanup system. SRI has assumed that 20 kWh/ton for this purpose, which is equivalent to 833 kWh/hr, or 7.8 million Btu/hr.

In summary, the process energy requirements are:

	10^6 Btu/hr
Loading	1.5
Air separation	28.2
System operation	7.8
	37.5

and the net energy available from the system is 235.02 - 37.5 or 197.5 million Btu/hr, which is equivalent to $197.5 \times 10^6/83,333$ = 2,370 Btu/lb of wet feed.

Pollution and Hazards

The Purox® system has one important waste stream -- the wastewater condensed from the converter offgas -- and two minor streams -- the slag and cooling tower blowdown. The slag, which should be primarily metals or metal silicates, should present no pollution or hazard problem. The blowdown is also minor and should pose no problem. Since little or no pesticide is used in the forests where the wood residue comes from, pesticide residue should not be a problem.

Land Disruption--

A small amount of land, no more than 0.06 acre/yr, need be dedicated to slag disposal. To accommodate the slag for the life of the plant, 1 acre was set aside for slag disposal. Union Carbide has estimated that a 1000 ton/day plant requires about 9.5 acres, including space for a Unox wastewater treatment system (estimated at 1.67 acres). SRI has assumed 9.5 acres is more than adequate for the plant, plus another 2 acres for storage of a week's supply of wood residue. If the plant operates

330 days/yr and provides gas with a net energy content of $1,560\times10^9$ Btu/yr (24 hr/day, 330 days/yr, 197.5 million Btu hr), the land requirements are 0.008 acre/10^9 Btu/yr (9.5 + 2 + 1/1560). If the wastewater treatment system is not included, land requirements reduce to 0.007 acre/10^9Btu/hr.

Air Emissions--

If the offgas is not dried and compressed and if electricity is the source of energy used to operate the plant, the only sources of emissions would be the exhaust gases from the loaders and fugitive particulate emissions from moving dusty material to and from storage and into the process. The amount of fugitive emissions depends on the method used and the care exercised, so those emissions cannot be quantified.

The estimated emissions from the two loaders and the total system are as follows:

	lb/hr
Carbon monoxide	2.7
Nitrogen oxide plus hydrocarbons	5.9

Large quantities (65,000 lb/hr) of nitrogen and carbon dioxide will be discharged from the air separation plant but neither are considered pollutants.

The contaminants in the offgas that are eventually burned are one indirect source, as are the emissions from the trucks used to deliver the wood residue to the plant. Another indirect source is the emission from power plants that supply the energy to operate the air separation plant, the Purox® system itself and, if required, the associated wastewater treatment system.

A summary of the direct environmental impact from the pyrolysis of wood residue via the Purox® process is provided in Table 42.

Water Pollution--

The two possible sources of water pollution from the Purox® system are the water condensed from the gas and leachate from the slag dump. The condensed water contains appreciable amounts of light organics, either steam-distilled from the wood or produced during pyrolysis. These organics are soluble in the condensed water and are too heavy to report to the gas stream.

Data provided by Union Carbide indicates that the organics are C_1 to C_4 aliphatics compounds and low molecular weight aromatics such as phenols, benezene, and furans. Unfortunately, the diversity of the compounds and the large dilution in the water makes recovery impractical.

In addition to the organic compounds, metallic substances are present in the wood and some are likely to be volatilized and end up in the wastewater. Table 43 shows the pounds per hour of minor elements in the

TABLE 42. ENVIRONMENTAL IMPACT OF PUROX® PYROLYSIS OF WOOD RESIDUE

Impact		Resource extraction	Onsite processing or storage	Transport to conversion plant	Conversion plant
Land disruption and use	Acres/ 10^9 Btu/ yr output				0.008
Water pollution					
Input	(gal/10^6 Btu)				1.25[a]
Output	(gal/10^6 Btu)				3.17[b]
Wasteheat	(gal/10^6 Btu)				0.29
Ammonia	(gal/10^6 Btu)				N/A
Phosphorus	(gal/10^6 Btu)				0
Salts	(gal/10^6 Btu)				negl.
Metals	(gal/10^6 Btu)				
Pesticides	(gal/10^6 Btu)				0
Air pollution					
NO_x	(lb/10^6 Btu)				[c]
SO_x	(lb/10^6 Btu)				negl.
H_2S	(lb/10^6 Btu)				0
Particulates	(lb/10^6 Btu)				negl.
Pesticides	(lb/10^6 Btu)				0
Hydrocarbons	(lb/10^6 Btu)				0.03
Carbon monoxide	(lb/10^6 Btu)				0.01
Organisms					0
Solid waste total	(lb/10^6 Btu)				1.6

[a] For adiabatic cooling only

[b] Includes condensed moisture from feed

[c] Included with hydrocarbons

wood residue feed and an estimate of the quantity and concentration likely to be in the slag and in the wastewater.

The chloride ion, if it reaches the 800^+ mg/ℓ concentration in the wastewater, could present a problem since the concentration would probably not be reduced by secondary treatment and the drinking water standard for the chloride ion is 250 mg/ℓ.

The concentration of zinc, 31 mg/ℓ, also exceeds the safe drinking water standard of 5 mg/ℓ. However, the zinc concentration could be reduced

TABLE 43. ESTIMATED DISPOSITION OF TRACE ELEMENTS IN WOOD RESIDUES FED TO PUROX® SYSTEM (lb/hr)

Element	Feed[a]	Slag[b]	Wastewater[b]	Concentration in wastewater (mg/ℓ)
Iron	108.3	NR[c]	NR	--
Chlorine[d]	56.7	14.2	42.5	815[e]
Zinc	14.6	13.0	1.6	31
Nickel	3.3	3.2	0.1	1.5
Manganese	58.3	58.3	0.01	0.1
Potassium	25.0	NR	NR	--
Vanadium	37.5	NR	NR	--
Chromium	2.9	2.9	0.002	negligible
Copper	2.1	2.1	0.0002	negligible
Cobalt	0.8	NR	NR	--

[a] Data from Georgia Tech

[b] Data from Union Carbide

[c] NR means not reported

[d] Based on statements made by Union Carbide -- organic chloride reports to wastewater and inorganic chloride reports to slag -- and data from Georgia Tech that shows 1/4 of chloride in wood ends up in the char.

[e] Union Carbide reports maximum chloride concentrations of 20 ppm in the condensate. Based on data from Georgia Tech, the wood residue contains over 0.1% chloride ion and 2/3 of this reports to the gaseous phase. Since very little, 1 ppm, is in the noncondensible gases, 2/3 must be in the condensate. So, chloride ion concentration must be much higher than reported in the Union Carbide tests.

during treatment to suitable levels. None of the other trace elements appear to present a pollution hazard or problem in the concentrations expected in the wastewater.

Leachate from the slag dump is another potential source of water pollution. Union Carbide had perimeter tests performed on their slag and some slag soil mixtures. Lead was the only element leached from the slag that exceeded the 0.05 mg/ℓ limit set for drinking water. Since lead is not reported as a trace element in wood residue (at least not in the residues tested by Georgia Tech), ground water contamination from slag-pile leachate appears to be no problem, at least as far as contaminating drinking water is concerned. However, there should be some soluble potassium and phosphate in the slag. Phosphate, in particular, can cause eutrophication if too much is allowed to enter surface waters, especially lakes or bays. Most soils absorb phosphates, so impoundment of any leachate should be sufficient to prevent phosphate contamination of surface waters.

TECH-AIR WITH RICE AND COTTON WASTES

The Tech-Air system should be able to process the mixed rice and cotton waste and do so more simply and economically than it can process wood waste. The moisture content of the rice hulls and straw (7 to 10%) appears low enough that drying can be eliminated. Even though the rice and cotton waste is less dense and probably does not flow as easily as the wood waste, experience with cotton gin trash as feed to the system indicates that mechanisms can be developed to make the waste move through the furnace efficiently and effectively.

Mass Balance

Predicting a mass balance for the system using rice and cotton waste, however, is another matter. Even though these wastes are composed of cellulose and lignin (just as are wood wastes), SRI cannot, based on the data available, estimate the weights or compositions of the products of pyrolysis with any reasonable degree of certainty.

This uncertainty stems, in part, from the difficulty Georgia Tech had trying to pyrolyze cotton gin trash. Even though the objective of that pyrolysis was to produce an oil fraction, they were unable to do so. This result is in marked contrast to the pyrolysis of wood, where the oil fraction was 6 to 20% of the feed. Another reason for the uncertainty is the differences between pulping of wood and rice. Rice straws are encased in a hard, noncellulosic skin. Removal of this skin in pulping of straws requires fairly drastic treatment with caustic. This skin could affect the rate and products of pyrolysis. The different heat transfer characteristics between the straw and wood could also affect the pyrolysis and the product mix.

Energy Balance

Without a product distribution, an energy balance cannot be developed.

Pollution and Hazards

As far as SRI knows, there is no published analysis that indicates the products formed when rice straws and hulls are pyrolyzed or distilled.

Land Disruption

Although minimal, the land use requirements are greater than for pyrolysis of wood residue because the feed is harvested in the third and fourth quarters of the year; up to 6 months' storage is needed.

Air Emission

The air emissions sources are the loader and motor-generator (if used). The emissions from these units would be the same as in the case of processing wood residue: 2.3 lb/hr of carbon monoxide and 5.1 lb/hr of NO_x. Except for possible pesticide residue, other pollutants are probably present in negligible amounts.

A summary of the environmental impacts cannot be provided as no data on net energy output could be developed.

PUROX® WITH RICE WASTE

The low bulk densities of rice hulls, and particularly rice straw, could cause problems in the Purox® converter unless changes are made. When compressed, refuse has a density of 40 to 50 lb/ft^3, which is probably twice as dense as the rice waste can be made. The mass of refuse moves from its own weight down the converter as the material at the bottom is melted or volatilized. Rice waste may not be dense enough to cause this same downward movement. Rice straw, because of its shape and density, is also more likely to cause bridging than is refuse. The burning characteristics of the rice waste may also be sufficiently different from refuse to cause problems. Revisions in the Purox® converter may be necessary and considerable experimentation may be required before the converter could operate satisfactorily using rice waste as a feed.

Mass Balance

Sufficient rice hulls and straws are available in the test area (Colusa, Sutter, and Butte Counties, California) to suggest a design of a plant to process 1000 tons/day of waste (three 350-ton/day Purox® converters in parallel) or 83,333 lb/hr.

The block flow diagram of the Purox® process, provided earlier in Figure 20, shows the processing of rice waste. The condensate, rather than being sent to a wastewater treatment plant for further processing, is distilled to recover the organics fraction.

The typical elemental analysis of ash and moisture content of the rice waste is different from the typical contents in refuse, as shown in Table 44.

TABLE 44. COMPARISONS OF RICE WASTE AND REFUSE COMPOSITION (wt %)

Element	Rice hulls and straw	Refuse
Carbon	35.5	29.0
Hydrogen	5.3	3.2
Nitrogen	0.5	N.A.[a]
Oxygen	36.7	22.8
Ash	14.4	17.9
Moisture	7.6	27.1

[a] Not available

Not only is the moisture content and ash lower and the organic matter (C + H + O) higher in the rice waste, but the organic fraction of rice waste contains more oxygen and hydrogen in relation to the carbon content than does the refuse. The basic composition of the rice waste is obviously different from the organic portion of refuse, so the products of decomposition are very likely to differ. Without some experimental data on product gas compositions, no reliable estimate can be made of the distribution of products that can be expected.

There are, however, some limits on the product composition. Obviously, the ash and moisture in the feed are products. Also, the composition of the offgases must be such that the energy released in the converter is just sufficient to: (1) heat the slag to its temperature of exit; (2) evaporate both the moisture in the feed and the water formed by the reactions in the converter; (3) heat the gases to their exit temperatures; and (4) provide for heat losses in and around the converter.

Even with this constraint, carbon, hydrogen, and oxygen can be distributed in many ways among the possible products. One such possible distribution is shown in Table 45. To achieve this distribution, 0.22 lb of oxygen is required per pound of waste. The elemental compositions and weights of each numbered flow on Figure 20 are shown in Table 46. (A small amount of sulfur is shown on Table 46, some of which is present in the offgases. The quantities are small and their form unknown (e.g., COS, H_2S, SO_2); they are not included in Table 45).

TABLE 45. ASSUMED OFFGAS COMPOSITION FROM RICE WASTE PYROLYSIS VIA PUROX® PROCESS

	lb/hr	Wt %	Vol % of dry, noncondensibles
Hydrogen	1,759.0	1.9	29.6
Carbon monoxide	25,657.1	28.3	30.8
Carbon dioxide	35,366.5	39.1	27.1
Methane (CH_4)	2,655.7	2.9	5.6
Acetylene (C_2H_2)	539.4	0.6	0.7
Ethylene (C_2H_4)	1,742.8	1.9	2.1
Ethane (C_2H_6)	266.8	0.3	0.3
C_3	634.3	0.7	0.5
C_4+	3,177.4	3.5	1.6
Oxygenated organics	177.8	0.2	0.2
H_2O from reaction	8,590.3	9.5	
Water-soluble organics	2,398.2	2.7	
Nitrogen	1,243.1	1.4	1.5
H_2O (moisture in feed)	6,329.1	7.0	
TOTAL	90,537.5	100	100

TABLE 46. PUROX® PROCESS STREAM FLOWS USING RICE WASTE FEED (1000 tons/day or 83.333 lb/hr)

	Stream	Carbon	Hydrogen	Nitrogen (and argon)	Oxygen	Sulfur	Ash	Refractory organic	Water	Total
Rice waste	1	29,596.43	4,383.83	387.33	30,634.45	1.54	12,000.28		6,329.14	83,333
Oxygen	2			855.81	18,350.52					19,206.33
Converter offgas	3	29,596.43	3,429.36	1,243.14	41,349.18	1.54		9,750.5	14,919.40	100,289.55
Slag	4						12,000.28			12,000.28
Spray water	5								20,000	20,000
Spray stream	6							9,750.5	17,967	27,717.5
Refractory organics	7							9,750.5		9,750.5
Wet offgas	8	29,596.43	3,429.36	1,243.14	41,349.18	1.54			16,952.4	92,572.05
Residue solids	9							n.a.[a]		n.a.[a]
Cool offgas	10	28,288.34	3,211.34	1,243.14	40,477.12	1.54			468.61	73,690.09
Condenser H_2O	11	1,308.09	218.02		872.06				16,483.79	18,881.96
Spray water discharge	12									
Wastewater treatment discharge	13	n.a.[a]	n.a.	n.a.	n.a.	--		--	n.a.	
Recovered organics	14	n.a.	n.a.	n.a.	n.a.	--		--	n.a.	

[a] Data not available; any solids, organic liquids, or water removed here would be recycled to stream.

As mentioned earlier, the process condensate is expected to contain nearly 13% (by weight) organics. This is much more concentrated than the condensate from the processing of wood residue, which would contain about 3% organics. Actually, the quantity of organic present in the condensate is about the same, but the amount of water in the wet gas from the converter processing of rice waste is much smaller than in the processing of wood residue. The condensate with a high concentration of organics could be steam-stripped to remove the organic portion for sale or use. The exact composition of the organic in the condensate is unknown, so the design of a system for its removal from the condensate cannot be provided. However, many of the organic compounds that could be present in the condenser should be separable from the water.

No data were found on the minor elements in the rice waste. Some data presented on Table 47 are available on a few of the minor constituents in rice hulls.

Of the elements listed on Table 47, only manganese and zinc appear to exhibit any volatility in the Purox® converter (see Mass Balance part of Purox® with Wood Residue section). Therefore, unless manganese and zinc or chromium or nickel are present in much higher concentrations in rice straw than in hulls, they should not cause handling or disposal problems.

TABLE 47. MINOR ELEMENTS REPORTED PRESENT IN RICE HULLS

Element	Wt % in hull
Silicon	7.7 to 8.5[a]
Potassium	0.2 to 0.7
Calcium	0.1 to 0.2
Sodium	0.01 to 0.02
Magnesium	0.04
Phosphorus	<0.04
Iron	<0.01
Copper	<0.006
Manganese	<0.001
Zinc	<0.001

[a] Based on silica content of rice hull ash.

Energy Balance

The energy balance about the converter (in millions of Btus per hour of operation) is as follows:

	lb/hr	Heat of combustion (Btu/lb)	10^6 Btu/hr In	10^6 Btu/hr Out
Feed	83,333	5,855[a]	487.9	
Gas				425.7
Organic in wastewater				25.6
TOTALS			487.9	451.3

---

[a] This is the theoretical heat of combustion estimated from the elemental composition of the rice wastes.

Of the energy available in the feed, as measured by the heats of combustion, 87% is still available in the fuel gas product. The 36.6 million Btu/hr consumed in processing performs the pyrolysis, evaporates the water, and heats the gases and the slag to their exit temperatures. It is much less than the energy required for pyrolyzing wood or refuse because the sensible heat in the water and slag leaving the converter is much less. If the wet gases leave the converter at 250°F and the slag at 2700°F, the sensible heat required would be as shown in Table 48.

The 10 million Btu/hr difference between the 36.6 million Btu/hr of energy consumed and the 26.6 million Btu/hr lost as sensible heat in the products is heat lost in and around the converter.

Energy is also consumed in processing of rice waste in the Purox® system to:

- Operate the air separation plant
- Load the waste into the system

TABLE 48. SENSIBLE HEAT REQUIREMENTS

	lb/hr	ΔH_{77}^{250} (Btu/lb)	Sensible heat (10^6 Btu/hr)
Water	14,920	1,118.9	16.69
Other gases	72,347	41.5	3.00
Liquified organics	2,398	175	0.42
Slag	12,000	540[a]	6.48
TOTALS	101,665		26.59

[a] ΔH_{77}^{2700}

- Drive the motors, fans, etc., required by the process itself
- Dry and compress the gas for pipelining

The air separation plant requires an estimated 2900 kW. The energy requirement for air separation is 27.2 million Btu/hr (assuming the 9400 Btu of fuel energy make 1 kWh of electricity).

The loading operation (83,300 lb/hr) can be accomplished with two 120-hp loaders, each consuming 6 gal/hr of diesel oil. Loading would require 1.5 million Btu/hr.

Since no definite figures are available for the converter and gas cleanup system energy requirements, SRI has assumed 20 kWh/ton for this purpose, which is equivalent to 833 kW or 7.8 million Btu/hr.

Since it is unlikely that a customer for the gas could be found so close that the gas could be piped directly to him, we assume that the gas would be compressed and dried for pipelining to customers 5 to 6 miles away.

The compression to 50 psi for such pipelining would require 3420 kW and the ethylene glycol stripping/reboiler unit would use 1.3% of the product gas to drive the abosrbed water from the ethylene glycol. The total energy required for compression (again assuming 9400 Btu/kWh) would be $32.15\text{x}10^6$ Btu/hr for compression and $4.63\text{x}10^6$ Btu/hr for drying.

The separation of some or most of the organic component from the condensate before discharge also requires an expenditure of energy, if undertaken. The amount of energy required can be estimated approximately. The condensate leaving the condenser is at about 100°F. The condensate must be reheated to its boiling point and the organics plus some water boiled off. Most organics in the wastewater have heats of vaporization around 150 Btu/lb. So the approximate energy expended per hour in separation is as follows:

	10^6 Btu/hr
Reheat 18,900 lb condensate to 212°F	2.12
Vaporize 90% of organics with a reflux (0.9)(2400)(150)(2) ratio of 1:1	0.64
Vaporize 5% of water with a reflux (16,500)(0.05)(970)(2) ratio of 1:1	1.60
Loses @ 40% of heat utilized (0.4)(4.36)	1.74
TOTAL	6.10

This energy could be supplied by burning part of the product gas. If this is done, the emissions would contain minor and probably harmless amounts of emissions other than water and carbon dioxide.

In summary, the process energy requirements are:

	10^6 Btu/hr
Loading	1.5
Air separation	27.2
System operation	7.8
Compression, pipelining	36.8
Organics recovery	6.1
TOTAL	79.4

and the net energy available from the system is 425.7 - 79.4, or 346.3 million Btu/hr, which is equivalent to 346.3/83,333 = 4,156 Btu/lb of rice waste feed.

Pollution and Hazards

Land Disruption--

More land is probably required on which to dispose of the slag from rice waste processing than from wood residue. About 48,000 tons/yr of slag or ash are produced, which requires about 13.8 acres/yr, assuming the bulk density of the ash is 9 lb/ft^3. (The bulk density of ash from rice hulls is reported[14] to be 6 to 12 lb/ft^3). The ash from a mixture of rice straw and hulls probably has about the same density). A plant with a 15-yr life needs just over 200 acres dedicated to slag disposal.

A number of uses have been proposed for rice hull ash. Among the considered proposals are the use of the ash as a reinforcement for rubber and as a substitute for part of the cement in concrete. The total elimination of the slag dump is possible if either of these uses were to develop.

The plant itself still requires about 9.5 acres. SRI has assumed that the compression plant increases this requirement by 1/2 acre.

Rice waste storage also requires additional space. One hundred percent of the rice hulls and straw are produced in the fourth quarter of the year. While part of the rice straw might be left in the field in January and February, by March the field must be prepared for the next season's crop. So storage for about 7 months of rice wastes (190,000 tons) must be provided if the plant is to operate continuously. Assuming a bulk density of 25 lb/ft^3, and a pile depth of 30 ft, another 12 acres would be required for feed storage.

The plant would be designed to operate 330 days/yr and to provide gas with a net energy content of 2743×10^9 Btu/yr (24 hr/day, 330 days/yr, 346.3×10^6 Btu/hr). The land requirements, assuming no use or better method of disposal for the ash, would be 222 acres or 0.08 acre/10^9 Btu/yr. If the ash can be used, the land requirement would be about 17 acres (feed = 12 acres, plant = 10 acres, product (ash) storage = 5 acres) or 0.01 acre/10^9 Btu/year.

Air Emissions--

The loading requirement for and the emissions from rice waste and wood residue are essentially the same: 6 lb/hr of hydrocarbons and NO_x, and 2 lb/hr of carbon monoxide.

Since the product gases must be dried and compressed and the waste stream separated into an organic-rich and a water-rich stream, additional process energy must be provided, which also produced pollutant emissions.

The quantities of emissions depend on the fuels used to supply the 6.1 million Btu/hr for condensate stripping and 5.02 million Btu for drying the ethylene glycol used as gas desicant. If No. 2 fuel oil (0.6% sulfur) is used, the emissions would be

Component	lb/hr
Particulates	1.3
Sulfur dioxide	6.9
Carbon monoxide	0.3
Hydrocarbons	0.3
Nitrogen oxides	4.8

If the converter offgas is used as the fuel instead of diesel oil, the emissions are much lower. Not all the emission data are available for such a case, but the following provides some of the information:

Component	Emissions from Purox® gas combustion to furnish process heat (lb/hr)
Particulates	0.03
Sulfur dioxide	0.08
Carbon monoxide	n.a.[a]
Hydrocarbons	n.a.[a]
Nitrogen oxides	n.a.[a]

[a] All emissions should be much less than from burning a comparable amount of diesel fuel oil.

Water Pollution--

As with the leachate from wood residue slag dumps, leachate from the rice waste slag dumps should not be a problem as long as the leachate is impounded and not allowed to flow directly into surface waters.

The water from the condenser will still contain some organic even if the majority of it is steam-stripped. By SRI's very preliminary approximation, the condenser water discharge of some 16,000 lb/hr (32 gpm) still includes about 240 lb of organics, probably mostly organic acids (formic, acetic, propionic, etc.) that are not readily separable from the water. Considering the small quantities involved and the need for water in the area where the rice wastes are generated, the most likely and effective disposition would be to use the condensate water for irrigation. If the BOD of the water is too high for it to be used directly for irrigation, it could be stored first in a lined or impervious stabilization pond.

Table 49 provides a summary of the information available on the known environmental impacts of pyrolyzing rice waste using the Purox® process.

TABLE 49. ENVIRONMENTAL IMPACTS OF PUROX® PYROLYSIS OF RICE WASTE

Impact		Resource extraction	Onsite processing or storage	Transport to conversion plant	Conversion plant
Land disruption and use	Acres/ 10^9 Btu/ yr output				0.08
Water pollution					
Input	(gal/10^6 Btu)				0.7[a]
Output	(gal/10^6 Btu)				5.4[b]
Wasteheat	(Btu/10^6 Btu)				0.06
Ammonia	(lb/10^6 Btu)				n.a.
Phosphorus	(lb/10^6 Btu)				0
Salts	(lb/10^6 Btu)				negl.
Metals	(lb/10^6 Btu)				0
Pesticides	(lb/10^6 Btu)				$3.5x10^{-5}$[c]
Air pollution					
NO_x	(lb/10^6 Btu)				0.014[d]
SO_x	(lb/10^6 Btu)				0.02[e]
H_2S	(lb/10^6 Btu)				negl.
Particulates	(lb/10^6 Btu)				0.004
Pesticides	(lb/10^6 Btu)				0
Hydrocarbons	(lb/10^6 Btu)				0.018[f]
Carbon monoxide	(lb/10^6 Btu)				0.01
Organisms					0
Solid waste total	(lb/10^6 Btu)				34.7

[a] For adiabatic cooling only.

[b] Includes condensed moisture from feed.

[c] Maximum possible quantity.

[d] Plus some NO_x included with hydrocarbons.

[e] Maximum quantity; could be as low as $8.7x10^{-5}$ lb/10^6 Btu.

[f] Includes some NO_x.

PUROX® WITH BARLEY AND COTTON WASTE

As indicated earlier, the quantities of these wastes available in Kern County, California are only sufficient to sustain the operation of a 750 ton/day Purox® plant. Except for size, the basic plant would be the same as the plant for processing rice waste. The basic flowsheet for that plant is shown in Figure 20.

The low bulk density of the barley and cotton waste feed could cause the same problems as was outlined for the case where rice wastes are used as feed.

Mass Balance

The typical analysis of the barley and cotton waste is also different than the typical analysis of refuse, as shown in Table 50.

TABLE 50. COMPARISONS OF BARLEY/COTTON WASTE AND REFUSE COMPOSITIONS (Wt %)

	Barley cotton	Refuse
Carbon	41.2	29.0
Hydrogen	5.6	3.2
Nitrogen	0.8	n.a.
Oxygen	39.6	22.8
Ash	5.3	17.9
Moisture	7.5	27.1

As with other agricultural waste, both the ash and moisture content are typically lower than in refuse. The barley and cotton waste also contains more hydrogen and oxygen in relation to carbon than does the refuse. These basic differences in composition mean again that no reliable estimate can be made of the expected distribution of products.

One possible distribution of reaction products, which takes into account the energy provided by the reaction and energy consumed through heat losses, is shown in Table 51.

To achieve the composition shown, 0.21 lb of oxygen is required per pound of waste.

The estimated elemental compositions and weights (in lb/hr) of each numbered flow on Figure 20 are shown in Table 52. As shown, the process condensate is expected to contain over 19% (by weight) organics. This is even more concentrated than the condensate from the processing of rice waste. A condensate with such a high organic content should be steam-stripped to remove as much as possible of the organic portion to sell

TABLE 51. ASSUMED OFFGAS COMPOSITION FROM BARLEY/COTTON WASTE PYROLYSIS VIA PUROX® PROCESS

	lb/hr	Wt %	Volume % (of dry noncondensibles)
Hydrogen	1,298.9	1.9	28.2
Carbon monoxide	19,431.3	28.6	30.1
Carbon dioxide	27,726.2	40.8	27.4
Methane (CH_4)	2,424.6	3.6	6.6
Acetylene (C_2H_2)	492.5	0.7	0.8
Ethylene (C_2H_4)	1,591.2	2.3	2.5
Ethane (C_3H_6)	243.5	0.4	0.4
C_3	579.1	0.8	0.6
C_4+	2,901.0	4.3	1.9
Oxygenated organics	162.4	0.2	0.2
H_2O (from reaction)	3,722.2	5.5	
Water-soluble organics	2,189.5	3.2	
Nitrogen	872.0	1.3	1.3
H_2O	4,375.0	6.4	
TOTAL	68,009.4	100.0	100.0

(possibly as a solvent) or use. The composition of the organics in the condensate is unknown; so, as with the condensate from the rice waste pyrolysis, the exact system design for removing the organics cannot be provided at this time. However, the probability is quite high that such a system can be designed and operated successfully.

No significant data were found on the minor elements in the barley and cotton waste. Calcium, magnesium, potassium, sodium and phosphate contents of barley straw are reported,[12] but these are present in very low concentrations and would end up in the ash. They should be considered neither toxic nor hazardous.

Energy Balance

The energy balance about the converter is as follows:

	lb/hr	Btu/lb	10^6 Btu/hr In	10^6 Btu/hr Out
Feed	58,333	6,721[a]	392.1	
Gas				346.8
Organic in wastewater				22.3
TOTAL			392.1	370.1

---

[a] This is the theoretical heat of combustion estimated from the elemental composition of barley/cotton waste.

TABLE 52. PUROX® PROCESS STREAM FLOWS USING BARLEY AND COTTON WASTE AS FEED

	Stream	Carbon	Hydrogen	Nitrogen (and argon)	Oxygen	Ash	Refractory organic	Water	Total
Barley/ cotton waste	1	24,065.4	3,237.5	485.6	23,094.2	3,075.6		4,375	58,333.3
Oxygen	2			386.4	12,365.3				12,751.7
Converter offgas	3	24,065.4	2,823.9	872.0	32,150.9		7,632.4	8,097.2	75,641.8
Slag	4					3,075.6			3,075.6
Spray water	5							13,500	13,500
Spray stream	6						7,632.4	12,138	19,770.4
Refractory organic	7						7,632.4		7,632.4
Wet offgas	8	24,065.4	2,823.9	872.0	32,150.9			9,459.2	69,371.4
Residue solids	9						n.a.[a]		n.a.[a]
Cool offgas	10	22,871.1	2,624.9	872.0	31,354.7			370.6	58,093.3
Condenser water	11	1,194.3	199.0	--	796.2			9,088.6	11,278.1
Spray water discharge	12								

[a] Data not available; any solids, organic liquids, or water removed here would be recycled to stream 6.

Thus, 88% of the energy available in the feed, as measured by the heats of combustion, is available in the fuel gas product. As in the other cases the 22 million Btu/hr performs the pyrolysis, evaporates the water and heats the bases and slag to their exit temperatures. The low moisture content and the small quantity of ash are the reasons why the pyrolysis of barley and cotton waste is so efficient (88%) because the sensible heat in the water and slag is low.

If the wet gases leave the converter at 250°F and the slag at 2700°F, the sensible heat required would be as shown in the following tabulation:

	lb/hr	ΔH_{77}^{250} Btu/lb	Lost sensible heat 10^6 Btu/hr
Water	8,097	1,118.9	9.06
Other gases	57,723	41.5	2.40
Liquified organics	2,189	175	0.38
Slag	3,076	540[a]	1.66
TOTAL	71,085		13.50

---

[a] ΔH_{77}^{2700}

Energy is also consumed to:

- Operate the air separation plant
- Load the waste into the system
- Drive the motors, fans, etc., required by the process itself
- Dry and compress the gas for pipelining

The air separation plant requires an estimated 200 kW. The energy requirement for air separation is 18.8 million Btu/hr (9400 Btu/1 kWh of electricity).

The loading operation (48,300 lb/hr) can be accomplished with two 90-hp loaders that each consume 4 gal/hr of diesel oil. The loading operation would require 1.1 million Btu/hr.

With no specific data on the energy requirements of the converter and gas cleanup system, SRI has assumed 20 kWh/ton, which is equivalent to 583 kW or 5.5 million Btu/hr.

SRI has assumed, as in the rice waste case, that the product gas must be dried, compressed and pipelined to customers 5 to 6 miles away.

The compression to 50 psi for pipelining would require about 2670 kW and the ethylene glycol stripping/reboiler would use 1% of the produced gas to drive the absorbed water from the ethylene glycol absorbant. (A smaller percentage of product gas -- 1.3% -- is needed to drive the reboiler/stripper than in the case of rice waste, because this gas has a higher Btu content -- 448 Btu/scf -- than the gas produced from rice wastes -- 342 Btu/scf). The total energy required for compression would be 25.10x10^6 Btu/hr for compression and 3.60x10^6 Btu/hr for drying.

The fractionation of the separable organic components from the condensate before discharge requires the following estimated amounts of energy (in 10^6 Btu/hr):

		10^6 Btu/hr
Reheat condensate from 100°F to 212°F (11278.1 lb/hr)(112°)	=	1.26
Vaporize 90% of organics, with 1:1 reflux ratio (0.9)(2189.5)(150)(2)	=	0.59
Vaporize 5% of water, with 1:1 reflux ratio (0.05)(9088.6)(970)(2)	=	0.88
Losses @ 40% of heat utilized (0.4)(2.73)	=	1.09
TOTAL		3.82

In summary, the process energy requirements are:

	10^6 Btu/hr
Loading	1.1
Air separation	18.8
System operation	5.5
Compression, pipelining	28.7
Organics recovery	3.8
TOTAL	57.9

The net energy available from the system is 346.8 - 57.9 or 289 10^6Btu/hr, which is equivalent to 289/58,333 or 4954 Btu/lb of barley and cotton waste feed.

Pollution and Hazards

Land Disruption--

About 12,000 tons/yr of slag or ash would be produced in processing the 750 tons/day of barley (330 days/yr). If this ash has the same density as ash from rice hulls, i.e., 9 lb/ft^3, about 3.5 acres/yr would be needed for disposal. A processing plant with a 15-yr life would need just over 50 acres dedicated to slag disposal.

The composition of this ash or slag is not known, although it certainly contains less silica than rice ash. Consequently, it probably could not be used for rubber reinforcement or as a cement additive. Since it does contain some phosphates and potash, it might be plowed back into the fields as a low value fertilizer. However, extensive testing of the ash/fertilizer concept would be required before the design of the plant without an area for ash disposal could be contemplated.

The plant itself, having a capacity of 750 tons/day, instead of 1000 tons/day as in the case of rice waste, would probably only require about 8 acres of land, including the land for the gas compression plant.

Storage of the waste prior to processing also requires additional space. All barley is harvested in June, the residue becoming available in July and August; all cotton is harvested in December, the residues becoming available in January and February. Under these circumstances, about 200,000 tons of waste may have to be stored at one time (in July or January).

Assuming a bulk density of 25 lb/ft^3 and a pile depth of 30 ft, another 13 acres would be required for feed storage.

The plant would be designed to operate 330 days/yr, and provide gas with a net energy content of 2289×10^9 Btu/yr (24 hr/day, 330 days/yr, 289×10^6 Btu/hr). The land requirements, assuming no use for the ash, would be 71 acres (50 acres for ash, 8 acres for plant, and 13 acres for feed) or 0.03 acre/10^9 Btu. If the ash can be used, the land requirement could be reduced to 21 acres, or 0.01 acre/10^9 Btu.

Air Emissions--

The two major potential sources of air pollution in the Purox® process operating on barley and cotton waste are: the exhausts from the loaders used to transfer the feed from storage to the converter; the burners used to provide heat to the condensate and heat to strip the water from the ethylene glycol absorbant. (Fugitive dust from the loading operation could also be a problem. To what extent this dust is a problem depends on the system devised and cannot be established at this time).

Two loaders with 90-hp diesel engines would emit:

4.4 lb/hr of NO_x plus hydrocarbons
2.0 lb/hr of carbon monoxide

The emissions from the condensate-stripper heaters depend on the fuel used. If No. 2 fuel oil (0.6% sulfur) is used, the emissions would be:

Component	lb/hr
Particulates	0.9
Sulfur dioxide	4.6
Carbon monoxide	0.2
Hydrocarbons	0.2
Nitrogen oxide	3.2

If converter offgas is used as the fuel instead of diesel oil, the emissions would be much lower. Actual emission data are not available. The particulate concentration in the offgas has been determined for the case where refuse is the feed. The particulate concentration using barley and cotton waste should be about the same. Based on that assumption, particulate emissions would be about 0.02 lb/hr. The emissions of all the other pollutants should also be much lower than from burning the diesel fuel oil.

Water Pollution--

The leachate from the slag made by processing barley and cotton waste should be very similar to leachate from rice waste slag. So, the leachate from barley and cotton slag dumps should not present a problem as long as the same precautions are exercised in preventing the leachate from entering surface waters directly.

The other possible source of water pollutants, the steam-stripped condensate, is again similar to the condensate from processing rice waste, at least as far as the BOD demand of the condensate is concerned. However, the pesticide content in the condensate is likely to be different.

Table 53 contains a summary of the known environmental impacts from pyrolyzing barley and cotton waste using the Purox® process.

TABLE 53. ENVIRONMENTAL IMPACTS OF PUROX® PYROLYSIS OF BARLEY AND COTTON WASTE

Impact		Resource extraction	Onsite processing or storage	Transport to conversion plant	Conversion plant
Land disruption and use	Acres/10^9 Btu/yr output				0.03
Water pollution					
Input	(gal/10^6 Btu)				0.6[a]
Output	(gal/10^6 Btu)				3.6[b]
Wasteheat	(Btu/10^6 Btu)				0.04
Ammonia	(lb 10^6 Btu)				n.a.
Phosphorus	(lb/10^6 Btu)				0
Salts	(lb/10^6 Btu)				negl.
Metals	(lb/10^6 Btu)				0
Pesticides	(lb/10^6 Btu)				n.a.
Air pollution					
NO_x	(lb/10^6 Btu)				0.026
SO_x	(lb/10^6 Btu)				0.016[c]
H_2S	(lb/10^6 Btu)				negl.
Particulates	(lb/10^6 Btu)				0.003
Pesticides	(lb/10^6 Btu)				0
Hydrocarbons	(lb/10^6 Btu)				0.001[d]
Carbon monoxide	(lb/10^6 Btu)				
Organisms					0
Solid waste total	(lb/10^6 Btu)				10.6

[a] For adiabatic cooling only.

[b] Includes condensed moisture from feed. Includes some hydrocarbons.

[c] Maximum quantity.

[d] Some hydrocarbon is included as part of NO_x.

APPENDIX A

ANAEROBIC DIGESTION - SUPPLEMENTAL DATA

INTRODUCTION

The information needed to evaluate the energy and pollution potentials of the anaerobic digestion process includes a mathematical model of the process and a raw material characterization of the agriculture waste. A mathematical model is developed first to describe waste degradation, methane production, and pollutant transport in the anaerobic process. Then, waste characteristics (including volatile solids content, nutrients, and heavy metals) are obtained from the literature. Tolerance levels for specific liquid phase constituents are assumed to allow estimation of purge stream flow. Using waste characteristics as input to the mathematical model, energy and pollution potentials can then be evaluated.

MATHEMATICAL MODEL FOR THE ANAEROBIC DIGESTION PROCESS

Process Model

The process model assumes a completely mixed digester with no solids recycled, as shown in Figure 6. The slurry feed to the digester is prepared by mixing water with agricultural waste to produce a solids concentration of 10%. To minimize wastewater generation and to conserve water and heat, as much water as possible is recirculated. The digested sludge solids that form from gravity settling are further dewatered by vacuum filtration to produce a cake with approximately 25% solids content.

Feed Slurry

Both biodegradable and refractory organics in the raw sludge can be expressed in terms of COD as follows:

$$S_d^o = f_d G X_t^o$$

$$S_r^o = (1 - f_d) G X_t^o$$

where

S_d^o = biodegradable COD in feed slurry (g/ℓ)

S_r^o = refractory COD in feed slurry (g/ℓ)

X_t^o = total suspended solids in feed slurry (g/ℓ)

G = ratio of COD to total suspended solids in feed slurry

f_d = biodegradable fraction of organic solids in feed slurry (assumed to be equivalent to biodegradable fraction of COD)

The total concentration of organic material in the feed slurry S_T^o can be expressed as the sum of S_d^o and S_r^o, i.e.,

$$S_T^o = S_d^o + S_r^o$$

Total suspended solids in the feed slurry consist of inorganic, biodegradable volatile, and refractory volatile suspended solids, i.e.,

$$X_t^o = X_{in}^o + X_d^o + X_r^o$$

$$X_{in}^o = (1 - f_v)X_t^o$$

$$X_d^o = f_d f_v X_t^o$$

$$X_r^o = (1 - f_d)f_v X_t^o$$

where

X_{in}^o = inorganic suspended solids in the feed slurry (g/ℓ)

X_d^o = biodegradable volatile suspended solids in the feed slurry (g/ℓ)

X_r^o = refractory volatile suspended solids in the feed slurry (g/ℓ)

f_v = fraction of total suspended solids that are volatile

Digested Slurry

A model has been developed[15] to describe the rate of waste usage in a biological reactor. According to this model, the concentration of biodegradable organics in the digested slurry S_d, can be expressed as:

$$S_d = \frac{K_s(1 + b\theta_c)}{\theta_c(Y_a k - b) - 1}$$

where

k = maximum specific substrate utilization rate by bacteria (g COD/g cells-day)

K_s = composite half-velocity coefficient for fatty acids (g/ℓ COD basis)

Y_a = yield coefficient for the rate-limiting-step organisms involved in the methane fermentation (g cells/g COD utilized)

b = microorganisms decay coefficient (day^{-1})

θ_c = digester solids detention time (day) = reactor detention time for case with no solids recycle

The concentration of refractory organics in the slurry S_r remains the same as that in the feed slurry, S_r^o, i.e.,

$$S_r = S_r^o$$

The concentration of active organisms X_a in the digested slurry can be expressed as:

$$X_a = \frac{Y\left(S_d^o - S_d\right)}{1 + b\theta_c}$$

where Y is the yield coefficient for overall waste decomposition (g cells/g COD utilized).

The concentration of refractory fraction of decayed organisms in the digested slurry X_{ar} can be written as:

$$X_{ar} = 0.2bX_a\theta_c$$

where the constant, 0.2, represents the refractory portion of the bacterial cells formed during cell decay.

The concentration of inorganic and refractory volatile suspended solids in the digested slurry remains the same as those in the feed slurry, i.e.,

$$X_{in} = X_{in}^o$$

$$X_r = X_r^o$$

The concentration of organic material in the digested slurry S_T consists of three portions: the remaining biodegradable and refractory portions of the original waste, S_d and S_r, plus the organic portion of the microorganisms. To add these together, the microorganism concentration must be expressed in COD units, rather than weight units, and so the conversion factor 1.42 is used:

$$S_T = S_d + S_r + 1.42(X_a + X_{ar})$$

The concentration of total suspended solids in the digested sludge X_t can be expressed as the sum of five components:

$$X_t = X_a + X_{ar} + X_{in} + X_r + X_d$$

Flow Rate and Digester Volume

Flow rate Q can be related to input rate of dry solids in agricultural wastes W and concentration of suspended solids in the feed slurry X_t^o as follows:

$$Q = \frac{W}{0.0623X_t^o}$$

where 0.0623 is a conversion factor;* Q is in ft³/day; W is in lb/day; X_t^o is in g/ℓ.

Volume of digester V can be expressed as the product of flow rate Q and solids detention time θ_c:

$$V = Q\theta_c$$

where V is in ft³; Q is in ft³/day; θ_c is in days.

Gross Methane Production

In anaerobic digestion, gross methane production can be directly correlated with COD reduction. According to McCarty[6], a reduction of 1 gram of COD is equivalent to the production of 0.35 liter of methane or 5.61 scf CH_4/lb COD. Using this relationship,

$$M_{gross} = 5.61Q(S_t^o - S_T)0.0623^*$$

where M_{gross} is the gross rate of gas production in scf per day.

Net Methane Production

To calculate net methane production, methane consumption for heating must be known. Heat loss of a digester can be calculated from the product of heat transfer coefficient, temperature difference and surface area. Assuming a cylindrical digester with a diameter of 110 ft and a depth of 35 ft (volume = 0.338×10^6 ft^3), the heat loss per digester from wall, top, and bottom can be calculated from the following relations:

---

*0.0623 is a conversion factor for g/ℓ to lb/ft³.

$$q_s = U_s(T - T_a)(24)(12{,}095)$$

$$q_t = U_t(T - T_a)(24)(9{,}503)$$

$$q_b = U_b(T - T_s)(24)(9{,}503)$$

where

q_s, q_t, q_b = heat loss from the sides, top, and bottom of each digester, respectively (Btu/day)

U_s, U_t, U_b = heat transfer coefficients for the sides, top, and bottom of each digester, respectively (Btu/hr-ft^2-day) assuming 2 inches foam insulation

T = temperature of digester, 95°F

T_a = temperature of air (°F)

T_s = temperature of soil (°F)

The total heat loss from a digester can be expressed as follows:

$$q_{loss} = (q_s + q_t + q_b)\left(\frac{V}{0.338 \times 10^6}\right)$$

where q_{loss} is in Btu/day and V is the total volume of all digesters required.

Heating requirement of a digester q_d can be calculated from the following relation, which assumes the density of slurry feed $\rho = 64$ lb/ft^3 and the specific heat of slurry feed $C_p = 1$ Btu/lb-°F. For the case without recycling,

$$q_d = Q \times 64 \times 1 \times (T - T^\circ)$$

where

q_d = digester heating requirement (Btu/day)

T° = temperature of feed slurry (°F)

For the case with recyling,

$$q_d = (Q - Q_{recycle}) \times 64 \times 1 \times (T - T°)$$

$$+ Q_{recycle} \times 64 \times 1 \times (T - T_{recycle})$$

where $Q_{recycle}$ is the flow rate of recycle stream in ft^3/day; $T_{recycle}$ is the temperature of recycle stream, chosen as 75°F based on the heat loss due to water evaporation in the vacuum filter operation of dewatering process.

The methane consumption for both heat loss and digester heating can be calculated by the following equation, assuming the fuel value of the methane is 960 Btu/scf CH_4, and the efficiency of methane utilization is 85%:

$$M_{consumption} = \frac{(q_d + q_{loss})}{(960)(0.85)}$$

where $M_{consumption}$ is in the unit of scf/day.

Net methane production equals gross methane production minus methane consumption:

$$M_{net} = M_{gross} - M_{consumption}$$

where M_{net}, M_{gross}, $M_{consumption}$ are all in the unit of scf/day.

Nutrient Requirements

The quantity of the biological nutrients, nitrogen and phosphorus, required by the microorganisms is directly proportional to their growth. The daily nitrogen and phosphorus requirement can be calculated by the following equations:[6]

$$N_{required} = 0.11X_aQ(0.0623)$$

$$P_{required} = 0.02X_aQ(0.0623)$$

where $N_{required}$ and $P_{required}$ are both in the unit of lb/day.

Distribution of Nutrients, Heavy Metals, and Solids in Dewatering Process

Many particulate nitrogen and phosphorus compounds are converted to soluble forms during anaerobic digestion.[16,17] The distribution of nutrients in digested sludge, settled sludge, and effluent has been reported.[18]

The results are as follows:

	Digested sludge (lb)	Settled sludge (lb)	Effluent (lb)
Nitrogen	14 (100%)	10.6 (76%)	3.4 (24%)
Phosphorus	8 (100%)	7.4 (93%)	0.6 (7%)

This study chose the following distribution coefficients for phosphorus in the dewatering step for the case without liquid recycling. Total nitrogen consists of soluble nitrogen (primarily NH_4-N) and nitrogen in solids. Since the concentration of soluble nitrogen is suspected to be nearly at the toxic level, the solubilization of nitrogen in solids is considered and is assumed to be in proportion to the biodegradation of organic solids. Heavy metals in digested sludge are commonly precipitated as sulfides and exist in the solid phase.[19,20] The distribution of heavy metals has been studied.[21] Based on the results of that study, the following distribution coefficient for heavy metals was chosen in dewatering for the case without liquid recycling:

Heavy metals	Digested sludge (%)	Cake (%)	Wastewater (%)
Copper Zinc Manganese Nickel Cadmium Mercury	100	70	30

The distribution for alkaline and earth alkaline metals is assumed to be the same as heavy metals.

For the case with liquid recycling, the quantities of nutrients, heavy metals, alkaline and earth alkaline metals in the dewatered solids are equal to the quantities in the feed slurry.

In this study, solids separation efficiency for dewatering process is assumed nearly 100%. The rate of solids output in cake can be expressed as follows:

$$W^e_{cake} = 0.0623 \times Q \times X^e_t$$

Numerical Values for Parameters in Process Model

The following data are used for heat loss and heating requirement calculation:

$$U_s = U_b = 0.12 \text{ Btu/(ft}^2\text{-hr-°F)}$$

$$U_t = 0.16 \text{ Btu/(ft}^2\text{-hr-°F)}$$

$$T_a = T_s = T^* = 50°F$$

For mesophilic digestion (T = 35°C, or 95°F), a solids retention time of $\theta_c = 20$ days was assumed, and the parameters for bacterial growth kinetics were chosen as follows:

$$k = 6.67 \text{ g COD/(g cells-day)}$$

$$K_s = 1.80 \text{ g COD/liter}$$

$$Y = 0.20 \text{ g cells/g COD utilized}$$

$$Y_a = 0.04 \text{ g cells/g COD utilized}$$

$$b = 0.03 \text{ day}^{-1}$$

RAW MATERIAL CHARACTERIZATION

Detailed characteristics of agricultural wastes can be found in publications.[12,22,23] Table A-1 summarizes characteristics for various agricultural wastes considered in this study. Five cases of digester feed are considered: (1) fresh cattle manure, (2) 5-month-old cattle manure, (3) fresh cattle manure and wheat residue, (4) chicken manure without liquid recycling, and (5) chicken manure with liquid recycling. In Table A-1, the values for parameters f_d, G and f_v are listed. Table A-2 explains the determination of their values.

MATERIAL AND ENERGY BALANCES

Energy and material balance calculations were carried out by using the raw material characterization data (Table A-1) and the process model. (Figure 8 showed energy production and consumption for various agriculture wastes.) Tables A-3 through A-7 present results of the material balances. Several points should be noted from analysis of these tables.

- The biodegradable fraction of volatile solids in cattle manure influences energy production significantly. This can be seen by comparing fresh manure and 5-month-old manure.
- Adding wheat residue to fresh manure does not increase net energy production. However, adding wheat residue can reduce the ammonia nitrogen concentration, which is only slightly below the assumed toxicity level (3,000 ppm), when fresh manure is used.
- In chicken manure, the solids concentration in the feed slurry is assumed to be 7% instead of 10%, as for cattle manure. This selection keeps the ammonium nitrogen below the assumed toxicity level.

When chicken manure is processed without liquid recycling, net energy production is negative, even though the ammonium nitrogen concentration is below the toxicity level. When chicken manure is processed with liquid recycling, but no nitrogen removal, the ammonium nitrogen exceeds the toxicity level, even though net energy production is positive. Therefore, the economic feasibility of using chicken manure as digester feed remains questionable.

TABLE A-1. WASTE CHARACTERISTICS

	Cattle manure, fresh	Cattle manure, 5-mo old	Wheat residue	Fresh cattle manure and wheat residue	Chicken manure
Quantities[a]	$2.20\text{x}10^{6}$	$1.41\text{x}10^{6}$[b]	$1.10\text{x}10^{6}$	$3.30\text{x}10^{6}$	$3.08\text{x}10^{6}$
Parameters					
G	1.0	0.9	1	1	0.86
f_d	0.60	0.31	0.1	0.43[d]	0.26
f_v	0.78	0.67	0.93	0.83[d]	0.77
Nutrients[a]					
Total N	$4.25\text{x}10^{4}$	$3.54\text{x}10^{4}$	–[c]	$4.25\text{x}10^{4}$	$1.85\text{x}10^{5}$
NH_4-N	$0.71\text{x}10^{4}$	0	–[c]	$0.71\text{x}10^{4}$	$1.18\text{x}10^{5}$
P	$1.15\text{x}10^{4}$	$1.15\text{x}10^{4}$	$4.84\text{x}10^{3}$	$1.63\text{x}10^{4}$	$5.88\text{x}10^{4}$
Alkaline[a] earth metals					
Na	$2.31\text{x}10^{3}$	$2.31\text{x}10^{3}$	–[c]	$2.31\text{x}10^{3}$	$1.17\text{x}10^{4}$
K	$3.77\text{x}10^{3}$	$3.77\text{x}10^{3}$	$4.68\text{x}10^{3}$	$4.24\text{x}10^{3}$	$6.16\text{x}10^{4}$
Ca	$5.63\text{x}10^{3}$	$5.63\text{x}10^{3}$	–[c]	$5.63\text{x}10^{3}$	$9.86\text{x}10^{4}$
Ma	$3.74\text{x}10^{3}$	$3.74\text{x}10^{3}$	–[c]	$3.74\text{x}10^{3}$	$1.48\text{x}10^{4}$
Heavy metals[a]					
Cu	13	13	–[c]	13	148
Zn	99	99	–[c]	99	$1.28\text{x}10^{3}$

[a] All values are in the unit of lb/day.

[b] See Table A-2. $\frac{\text{5.8 lb dry solids/head (5-mo. cycle)}}{\text{9 lb dry solids/head (fresh)}} = 0.64.$

[c] Data are not found in literature and are believed to be negligible compared to those of fresh cattle manure.

[d] $f_v = (1.1/3.3)(0.93) + (2.2/3.3)(0.78) = 0.83$

$f_d = (1.1/3.3)(0.1) + (2.2/3.3)(0.6) = 0.43$

TABLE A-2. SUMMARY OF ASSUMPTIONS FOR DETERMINING f_v, G,[a] AND f_d[b]

CATTLE MANURE: per 900 lb (410 kg) steer (following based on data from Reference 22)

Quantity, fresh:[c]

60 lb (30 kg) wet manure/day	43 lb feces (20 kg) 17 lb urine (8 kg)
9 lb (4.1 kg) dry manure/day or 7 lb (3.2 kg) volatile solids/day	1.5 lb BOD_5 (0.68 kg) 9 lb COD (4.1 kg)
9 lb (4.1 kg) dry manure/day	2.0 lb (0.91 kg) inorganics 2.8 lb (1.3 kg) nondegradable org. 4.2 lb (1.9 kg) degradable organics

Volatile fraction of dry solids = 0.78

Quantity, 5-month collection cycle:

5.8 lb (2.6 kg) dry manure/day	1.9 lb (0.86 kg) inorganics 2.7 lb (1.2 kg) nondegradable org. 1.2 lb (0.55 kg) degradable organics

Volatile fraction of dry solids = 0.67

Calculation of G:

Manure, fresh:

$$G = 9 \text{ lb COD}/9 \text{ lb dry manure} = 1$$

and 7 lb organics/9 lb dry manure

Therefore: 1.29 lb COD/lb organic

Manure, 5-month collection cycle:

$$G = \frac{4.1 \text{ lb organics}}{5.8 \text{ lb dry manure}} \; \frac{1.29 \text{ lb COD}}{\text{lb organics}}$$

$$= 0.91 \text{ lb COD/lb dry manure}$$

---

[a] G = mass COD/mass dry solids

[b] f_d = fraction of organic solids that is degradable (assumed equal to degradable fraction of COD)

[c] Fresh manure (defined by SRI to be less than 1 month old)

TABLE A-2 (continued)

CATTLE MANURE: (continued)

Calculation of f_d:

Manure, fresh: $$f_d = \frac{4.2 \text{ lb degradable organics}}{7 \text{ lb organics}} = 0.60$$

Manure, 5-month collection cycle: $$f_d = \frac{1.2 \text{ lb/degradable organics}}{3.9 \text{ lb organics}} = 0.31$$

WHEAT:

Calculation of G:

Assumed wheat composition:

Moisture	18 wt %
Ash	5.5 wt %
Volatile solids or organics	76.5 wt %
Volatile fraction of dry solids	0.93 (f_v)

$$G = \frac{76.5 \text{ lb } (CH_2O)}{82 \text{ lb dry straw solids}} \times \frac{8 \text{ lb COD}}{7.5 \text{ lb } CH_2O} = 1$$

Calculation of f_d:

Digestible fraction of cellulose in wheat straw approximately = 25%.
(Reference 23)
Fraction of cellulose in wheat straw approximately = 40% on dry basis.
$f_d \cong 0.25 \times 0.40 = 0.1$.

CHICKEN MANURE: (per animal from Reference 12)

Quantity, fresh:

$$0.25 \text{ lb wet manure/day} \begin{cases} 0.066 \text{ lb dry solids} \\ 0.051 \text{ lb organics} \\ 0.015 \text{ lb inorganics} \end{cases}$$

$$0.051 \text{ lb organics/day} \begin{cases} 0.057 \text{ lb COD} \\ \\ 0.015 \text{ lb BOD} \end{cases}$$

Volatile fraction of dry solids = 0.77 (f_v)

TABLE A-2 (continued)

CHICKEN MANURE: (continued)

Calculation of G:

$$G = \frac{0.057 \text{ lb COD}}{0.066 \text{ lb dry solids}} = 0.86$$

Calculation of f_d:

$$f_d = \frac{0.015 \text{ lb BOD}}{0.057 \text{ lb COD}} = 0.26$$

TABLE A-3. MATERIAL BALANCE FOR FRESH CATTLE MANURE AS DIGESTER FEED WITH LIQUID RECYCLING (lb/day)

	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6	Stream 7	Stream 8	Stream 9	Stream 10
Dry solids	2.20×10^6		2.20×10^6				1.35×10^6	1.35×10^6		
Water	0.88×10^7	0	1.98×10^7				1.98×10^7	0.41×10^7	0.47×10^7	1.10×10^7
Nutrients										
Total N	4.25×10^4		7.25×10^4				7.25×10^4	2.97×10^4	1.28×10^4	3.0×10^4
Soluble - N	0.71×10^4		3.71×10^4				5.39×10^4	1.11×10^4	1.28×10^4	3.0×10^4
Solids - N	3.54×10^4		3.54×10^4				1.86×10^4	1.86×10^4		
Total P	1.15×10^4							1.15×10^4		
Alkaline earth metals										
Na	2.31×10^3							2.31×10^3		
K	3.77×10^4							3.77×10^4		
Ca	5.63×10^3							5.63×10^3		
Mg	3.74×10^3							3.74×10^3		
Heavy metals										
Cu	13							13		
Zn	99							99		
Methane (scf/day)				5.81×10^6	1.15×10^6	4.66×10^6				

TABLE A-4. MATERIAL BALANCE FOR FIVE-MONTH-OLD CATTLE MANURE AS DIGESTER FEED WITH LIQUID RECYCLING
(lb/day)

	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6	Stream 7	Stream 8	Stream 9	Stream 10
Dry solids	1.41×10^6		1.41×10^6				1.18×10^6	1.18×10^6		
Water	0.41×10^7	0.21×10^7	1.27×10^7				1.27×10^7	0.35×10^7	0	0.92×10^7
Nutrients										
Total N	3.54×10^4		5.01×10^4				5.01×10^4	3.54×10^4		1.47×10^4
NH_4-N	0		1.47×10^4				2.03×10^4	0.56×10^4		1.47×10^4
Solids - N	3.54×10^4		3.54×10^4				2.98×10^4	2.98×10^4		
Total P	1.15×10^4							1.15×10^4		
Alkaline earth metals										
Na	2.31×10^3							2.31×10^3		
K	3.77×10^4							3.77×10^4		
Ca	5.63×10^3							5.65×10^3		
Mg	3.74×10^3							3.74×10^3		
Heavy metals										
Cu	13							13		
Zn	99							99		
Methane (scf/day)				2.14×10^6	0.74×10^6	1.40×10^6				

TABLE A-5. MATERIAL BALANCE FOR FRESH MANURE AND WHEAT RESIDUE AS DIGESTER FEED WITH LIQUID RECYCLING (lb/day)

	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6	Stream 7	Stream 8	Stream 9	Stream 10
Dry solids	$3.30x10^6$		$3.30x10^6$				$2.33x10^6$	$2.33x10^6$		
Water	$0.89x10^7$	0	$2.97x10^7$				$2.97x10^7$	$0.70x10^7$	$0.19x10^7$	$2.08x10^7$
Nutrients										
Total N	$4.25x10^4$		$8.71x10^4$				$8.71x10^4$	$4.25x10^4$	$0.41x10^4$	$4.46x10^4$
Soluble - N	$0.71x10^4$		$5.17x10^4$				$6.37x10^4$	$1.50x10^4$	$0.41x10^4$	$4.46x10^4$
Solids - N	$3.54x10^4$		$3.54x10^4$				$2.34x10^4$	$2.34x10^4$		
Total P	$1.63x10^4$							$1.63x10^4$		
Alkaline earth metals										
Na	$2.31x10^3$							$2.31x10^3$		
K	$4.24x10^4$							$4.24x10^4$		
Ca	$5.63x10^3$							$5.63x10^3$		
Mg	$3.74x10^3$							$3.74x10^3$		
Heavy metals										
Ca	13							13		
Zn	99							99		
Methane (scf/day)				$6.31x10^6$	$1.63x10^6$	$4.68x10^6$				

TABLE A-6. MATERIAL BALANCE FOR CHICKEN MANURE AS DIGESTER FEED WITHOUT LIQUID RECYCLING
(lb/day)

	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6	Stream 7	Stream 8	Stream 9	Stream 10
Dry solids	3.08×10^{6}		3.08×10^{6}				2.60×10^{6}	2.60×10^{6}		
Water	0.31×10^{7}	3.78×10^{7}	4.09×10^{7}				4.09×10^{7}	0.78×10^{7}	3.31×10^{7}	0
Nutrients										
Total N	1.85×10^{5}		1.85×10^{5}				1.85×10^{5}	0.79×10^{5}	1.06×10^{5}	
NH_4-N	1.18×10^{5}		1.18×10^{5}				1.31×10^{5}	0.25×10^{5}	1.06×10^{5}	
Solids - N	0.67×10^{5}		0.67×10^{5}				0.54×10^{5}	0.54×10^{5}		
Total P	5.88×10^{4}		5.88×10^{4}				5.88×10^{4}	5.47×10^{4}	0.41×10^{4}	
Alkaline earth metals										
Na	1.17×10^{4}		1.17×10^{4}				1.17×10^{4}	0.82×10^{4}	0.35×10^{4}	
K	6.16×10^{4}		6.16×10^{4}				6.16×10^{4}	4.31×10^{4}	1.85×10^{4}	
Ca	9.86×10^{4}		9.86×10^{4}				9.86×10^{4}	6.90×10^{4}	2.96×10^{4}	
Mg	1.48×10^{4}		1.48×10^{4}				1.48×10^{4}	1.04×10^{4}	0.44×10^{4}	
Heavy metals										
Cu	148		148				148	104	44	
Zn	1.28×10^{3}		1.28×10^{3}				1.28×10^{3}	0.90×10^{3}	0.38×10^{3}	
Methane (scf/day)				2.97×10^{6}	3.04×10^{6}	-0.07×10^{6}				

TABLE A-7. MATERIAL BALANCE FOR CHICKEN MANURE AS DIGESTER FEED WITH LIQUID RECYCLING
(lb/day)

	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6	Stream 7	Stream 8	Stream 9	Stream 10
Dry solids	3.08x10^{6}		3.08x10^{6}				2.60x10^{6}	2.60x10^{6}		
Water	0.31x10^{6}	0.47x10^{7}	4.09x10^{7}				4.09x10^{7}	0.78x10^{7}	0	3.31x10^{7}
Nutrients										
Total N	1.85x10^{5}		7.41x10^{5}				7.41x10^{5}	1.85x10^{5}		5.56x10^{5}
NH$_4$-N	1.18x10^{5}		6.74x10^{5}				6.87x10^{5}	1.31x10^{5}		5.56x10^{5}
Solids - N	0.67x10^{5}		0.67x10^{5}				0.54x10^{5}	0.54x10^{5}		
Total P	5.88x10^{4}							5.88x10^{4}		
Alkaline earth metals										
Na	1.17x10^{4}							1.17x10^{4}		
K	6.16x10^{4}							6.16x10^{4}		
Ca	9.86x10^{4}							9.86x10^{4}		
Mg	1.48x10^{4}							1.48x10^{4}		
Heavy metals										
Cu	148							148		
Zn	1.28x10^{3}							1.28x10^{3}		
Methane (scf/day)				2.97x10^{6}	2.02x10^{6}	0.95x10^{6}				

ENVIRONMENTAL CONSIDERATIONS

Sulfur and nitrogen emissions have been considered in this study due to the combustion of produced gas for digestion system heating. For most anaerobic digesters,[24] hydrogen sulfide is usually not above 100 grains/100 ft^3 of gas, or, 205 lb of sulfur/1,000,000 ft^3 of methane produced. This emission factor was used to estimate sulfur dioxide emissions from the boiler per day and sulfur dioxide emissions per net million Btu produced for various cases of agricultural waste.

Nitrogen oxides emissions from the boiler depend on the ammonia (NH_3) concentration in the produced gas, which varies with the *p*H of the digestion slurry. For a *p*H around 7.5, the NH_3 concentration in the gas is 2% of total ammonium-nitrogen concentration. Using this factor and the ammonium-nitrogen concentration in the digestion slurry, the digester gas ammonia concentrations were estimated and the nitrogen oxides emissions from the boiler were calculated.

Tables A-8 and A-9 present sulfur dioxide and nitrogen oxides emissions per day and per net million Btu produced for various agricultural wastes.

TABLE A-8. SULFUR AND NITROGEN EMISSION PER 10^6 Btu NET SUPPLY PRODUCTION FOR ANAEROBIC DIGESTION PROCESS

	Sulfur emission ($lb\ S/10^6$ Btu)	Nitrogen emission ($lb\ N/10^6$ Btu)
Fresh cattle manure	0.054[0.108][a]	0.049[0.161][b]
Cattle manure (5-month collection cycle)	0.11[0.22][a]	0.057[0.187][b]
Fresh cattle manure and wheat residue	0.074[0.148][a]	0.052[0.171][b]
Chicken manure without liquid recycling	-	-
Chicken manure with liquid recycling	0.45[0.90][a]	0.57[1.87][b]

[a] Unit is lb $SO_2/10^6$ Btu.

[b] Unit is lb $NO_2/10^6$ Btu.

If the digester solids are separated by a vacuum filter, then an H_2S laden gas stream would be emitted from the vacuum pump. This analysis assumes that the exhaust gas from the vacuum pump is treated for H_2S removal by one of the following processes:

- Scrubbing and subsequent liquid phase oxidation
- Air oxidation on a bed of activated carbon
- Air oxidation on a bed of iron oxide

In any of the above cases, the H_2S emissions should be reduced to a very low level. Ammonia removal would be achieved only by use of an acid-scrubbing solution following the above devices.

H_2S in the product gas would be removed before sales to a pipeline gas company, but this has not been considered in this analysis. The gas burned for digester heating is as received from the digesters and NO_x and SO_x emission levels have been calculated and listed in Tables A-8 and A-9.

TABLE A-9. SULFUR AND NITROGEN EMISSION PER DAY FOR ANAEROBIC DIGESTION PROCESS

	Sulfur emission (lb S/day)	Nitrogen emission (lb N/day)
Fresh cattle manure	240	218
Cattle manure (5-month collection cycle)	152	76
Fresh cattle manure and wheat residue	334	235
Chicken manure without liquid recycling	623	246
Chicken manure with liquid recycling	414	517

APPENDIX B

ENVIRONMENTAL ANALYSIS ASSUMPTIONS, CALCULATIONS,[a] AND DATA SUMMARY

TABLE B-1. COAL-FIRED POWER PLANT EMISSIONS TO AIR
(Power plant with low-sulfur coal and flue gas desulfurization)

Thermal efficiency	~40%
Coal heating value	9000 Btu/lb
Coal sulfur content	0.81%
Plant heat rate	8500 Btu/kWh
Flue gas desulfurization	85% SO_2 removal

SO_2 emitted:

$$\frac{\frac{8500\ \text{Btu}}{\text{kWh}} \times \frac{0.01\ \text{lb S}}{\text{lb coal}} \times \frac{2\ \text{lb SO}_2}{\text{lb S}} \times 0.15}{\frac{9000\ \text{Btu}}{\text{lb coal}}} = \frac{0.0028\ \text{lb SO}_2}{\text{kWh}}$$

$$\text{or} \quad \frac{0.0028\ \text{lb SO}_2}{3414\ \text{Btu output}} = \frac{0.83\ \text{lb SO}_2}{10^6\ \text{Btu output}}{}^{b}$$

Particulate collection efficiency	99.7%
Coal ash content	20%
Fly ash/bottom ash	4/1

Fly ash emitted:

$$\frac{\frac{8500\ \text{Btu}}{\text{kWh}}\ \frac{0.2\ \text{lb ash}}{\text{lb coal}}\ \frac{0.8\ \text{lb fly ash}}{\text{lb ash}}\ \frac{0.005\ \text{lb emitted}}{\text{lb fly ash}}}{\frac{9000\ \text{Btu}}{\text{lb coal}}} = \frac{4.5\text{x}10^{-4}\ \text{lb}}{\text{kWh}}$$

$$\text{or} \quad \frac{0.13\ \text{lb}}{10^6\ \text{Btu output}}$$

NO_x emitted (source): $\frac{0.007\ \text{lb}}{\text{kWh}}$ or $\frac{1\ \text{lb}}{10^6\ \text{Btu output}}$

---

[a] Some background information and data for the calculations contained in this appendix were taken from References 25, 26, and 27.

[b] NSPS of 1.2 lb $SO_2/10^6$ Btu fired equivalent to approx 3 lb $SO_2/10^6$ Btu output so that this example plant is far superior to one meeting NSPS.

TABLE B-2. WATER REQUIREMENTS FOR COAL-FIRED POWER PLANT

POWER PLANT COOLING TOWERS:

Heat rate	8500	Btu/kWh
	-3414	
Total heat rejected	5086	
Plant heat loss (12% of heat rate)	-1017	
Heat rejected by cooling tower	4069	

$$\frac{4069\ \text{Btu/kWh}}{1000\ \text{Btu/lb}\ H_2O} = \frac{4.1\ \text{lb}\ H_2O}{\text{kWh}}$$

$$\frac{1200\ \text{lb}\ H_2O}{10^6\ \text{Btu output}} \quad \text{or} \quad \frac{144\ \text{gal}}{10^6\ \text{Btu output}}$$

POWER PLANT SCRUBBERS:

Water with waste sludge and ash > 1 lb H_2O/lb solids:

$$\frac{1\ \text{lb}\ H_2O}{\text{lb solids}} \times \frac{54\ \text{lb solids}}{10^6\ \text{Btu output}} = \frac{54\ \text{lb}\ H_2O}{10^6\ \text{Btu output}} = \frac{6.5\ \text{gal}}{10^6\ \text{Btu output}}$$

Water evaporated in scrubber (75% of plant heat loss for evaporative cooling of gas in scrubber):

$$\frac{763\ \text{Btu/kWh}}{1000\ \text{Btu/lb}\ H_2O} = \frac{0.76\ \text{lb}}{\text{kWh}}$$

$$\frac{222\ \text{lb}\ H_2O}{10^6\ \text{Btu output}} \quad \text{or} \quad \frac{27\ \text{gal}}{10^6\ \text{Btu output}}$$

Cooling tower	~144 gal/10^6 Btu output
Scrubbers (evaporation)	27 gal/10^6 Btu output
(sludge)	7 gal/10^6 Btu output
Miscellaneous	22 gal/10^6 Btu output
Total	200 gal/10^6 Btu output

Wastewater - Assume water in cooling tower is concentrated five-fold in salt content and that blowdown is used for scrubbers. Tower blowdown is about 46 gal/10^6 Btu output.

TABLE B-3. COAL-FIRED POWER PLANT SYSTEM EMISSIONS AND LAND DISTURBANCE

LAND	
Mining land disruption	15.2 acres/10^9 Btu output/day
Coal cleaning land requirements	0.65 acre/10^9 Btu output/day
Conversion land requirements	15.3 acres/10^9 Btu output/day
WATER POLLUTION	
Mining - silt runoff	0.25 lb/10^6 Btu output
Conversion - minimal - assume all blowdown from cooling towers and other streams goes to evaporation ponds	
SOLID WASTE (dry basis)	
Mining	Assume = 0 with all returned to mine
Conversion plant (ash + FGD solids)	54 lb/10^6 Btu output
AIR POLLUTION	
Coal cleaning	0.01 lb/10^6 Btu output
Conversion or power plant	See Table B-1

TABLE B-4. COAL COMBUSTION FOR ELECTRIC POWER GENERATION

Impact		Resource extraction	Onsite processing or storage	Transport to conversion plant	Conversion plant
Land disruption and use	Acres/ 10^9 Btu/ day output	15.2	0.65	Neg.	15.3
Water pollution					
Input	(gal/10^6 Btu)	4 to 8	0	0	200
Output[a]	(gal/10^6 Btu)	Neg.	0	0	8
Ammonia	(lb/10^6 Btu)	0	0	0	0
Phosphorus	(lb/10^6 Btu)	0	0	0	0
Salts	(lb/10^6 Btu)	0	0	0	0
Metals	(lb/10^6 Btu)	0	0	0	0
Pesticides	(lb/10^6 Btu)	0	0	0	0
Silt	(lb/10^6 Btu)	0.25	0	0	0
Air pollution					
NO_x	(lb/10^6 Btu)	Neg.	0	Neg.	2.0
SO_x	(lb/10^6 Btu)	Neg.	0	Neg.	0.83
H_2S	(lb/10^6 Btu)	Neg.	0	Neg.	--
Particulates	(lb/10^6 Btu)	Neg.	0.01	Neg.	0.13
Pesticides	(lb/10^6 Btu)	0	0	0	0
Organisms		0	0	0	0
Solid waste total	(lb/10^6 Btu)	0	0	0	54

[a] Assume all wastewater goes to evaporation ponds with no discharge.

TABLE B-5. COAL GASIFICATION WITH LURGI TECHNOLOGY[a]

Gas production	~250x10^{6} scf/day or 250x10^{9} Btu/day
Liquids production	~50x10^{9} Btu/day
Purchased electric power	1.15x10^{6} kWh/day
Power plant input energy	9.8x10^{9} Btu/day
Net energy output	~290x10^{9} Btu/day
Total plant SO_2 emissions	30,000 lb/day or $\frac{0.10\ \text{lb}\ SO_2}{10^6\ \text{Btu output}}$
Total plant NO_x emissions	720 lb/day or $\frac{0.0025\ \text{lb}}{10^6\ \text{Btu output}}$
Total plant particulate emissions	3600 lb/day or $\frac{0.012\ \text{lb}}{10^6\ \text{Btu output}}$

Mining and hauling emissions

Particulate	1.5x10^{-4} lb/10^{6} Btu output
SO_2	3.1x10^{-4} lb/10^{6} Btu output
NO_x	4.2x10^{-3} lb/10^{6} Btu output

[a] Proposed by Pacific Coal Gasification Company and Transwestern Coal Gasification Company.

TABLE B-6. WATER REQUIREMENTS FOR COAL GASIFICATION USING LURGI TECHNOLOGY

Assume 67% of heat load dissipated by air cooling.

Intake water - 5,100 gal/min (7.344x10^{6} gal/day)
or 25.3 gal/10^{6} Btu output.

Water discharge to evaporation ponds or deep wells in western areas will be ≤2x10^{6} gal/day or 6.9 gal/10^{6} Btu output.

TABLE B-7. LURGI COAL GASIFICATION PLANT EMISSIONS AND LAND DISTURBANCES

LAND	
Mining land disruption	1.9 acres/10^9 Btu/day
Coal cleaning and mining support	1.3 acres/10^9 Btu/day
Conversion plant	2 acres/10^9 Btu/day
WATER POLLUTION	
Mining - silt runoff	0.25 lb/10^6 Btu output
Conversion	See Table
SOLID WASTE	
(Ash, water treatment solids, biological solids, FGD scrubber sludge, boiler ash) 6,869 ton/day or 47 lb/10^6 Btu output	

TABLE B-8. COAL GASIFICATION[a]

Impact		Resource extraction	Onsite processing or storage	Transport to conversion plant	Conversion plant
Land disruption and use	Acres/ 10^9 Btu/ day output	1.9	1.0	0.3	2.0
Water pollution					
Input	(gal/10^6 Btu)	3 to 4	0	0	25
Output[b]	(gal/10^6 Btu)	0	0	0	≤ 6.9
Ammonia	(lb/10^6 Btu)	0	0	0	NA
Phosphorus	(lb/10^6 Btu)	0	0	0	NA
Salts	(lb/10^6 Btu)	0	0	0	NA
Metals	(lb/10^6 Btu)	0	0	0	NA
Pesticides	(lb/10^6 Btu)	0	0	0	--
Silt	(lb/10^6 Btu)	0.04	--	--	--
Air pollution (no fugitive emissions included)					
NO_x	(lb/10^6 Btu)	0.002	0	0.003	0.0025
SO_x	(lb/10^6 Btu)	0.00015	0	0.0002	0.10
H_2S	(lb/10^6 Btu)	--	0	--	
Particulates	(lb/10^6 Btu)	0.00007	0.04	0.0001	0.012
Pesticides	(lb/10^6 Btu)	--	0	--	--
Solid waste total	(lb/10^6 Btu)	0	0	0	47

[a] Basis: 250 million scf/day of methane, Lurgi technology assuming Northwestern New Mexico site as proposed by El Paso and WESCO.

[b] Assume all wastewater goes to evaporation pond or deep well.

Noise: 85-90 dBA at gasification plant boundary 660 ft from accoustical center; comparable levels for coal preparation plant; blasting noise at mine and vehicle noise in mining areas and on haul roads.

TABLE B-9. ANAEROBIC DIGESTION[a]
(Case 1-A)

Impact		Resource extraction	Onsite processing or storage	Transport to conversion plant	Conversion plant
Land disruption and use	Acres/ 10^9 Btu/ day output	0	0	0	4.7 + 25 for evap. pond
Water pollution					
Input	(gal/10^6 Btu)	0	0	0	0
Output	(gal/10^6 Btu)	0	0	0	[b]
Ammonia	(lb/10^6 Btu)	0	0	0	0
Phosphorus	(lb/10^6 Btu)	0	0	0	0
Salts	(lb/10^6 Btu)	0	0	0	0
Metals	(lb/10^6 Btu)	0	0	0	0
Pesticides	(lb/10^6 Btu)	0	0	0	0
Air pollution					
NO_x	(lb/10^6 Btu)	0	0	0	0.16
SO_x	(lb/10^6 Btu)	0	0	0	0.18
H_2S	(lb/10^6 Btu)	0	0	0	Neg.
Particulates	(lb/10^6 Btu)	0	0	0	Neg.
Pesticides	(lb/10^6 Btu)	0	0	0	0
Solid waste total	(lb/10^6 Btu)	0	0	0	Neg.

[a] Basis: Fresh cattle manure with liquid recycle.

[b] All wastewater goes to evaporation pond.

TABLE B-10. ANAEROBIC DIGESTION[a]
(Case 1-B)

Impact		Resource extraction	Onsite processing or storage	Transport to conversion plant	Conversion plant
Land disruption and use	Acres/ 10^9 Btu/ day output	0	0	0	15.6
Water pollution					
Input	(gal/10^6 Btu)	0	0	0	187
Output	(gal/10^6 Btu)	0	0	0	0
Ammonia	(lb/10^6 Btu)	0	0	0	0
Phosphorus	(lb/10^6 Btu)	0	0	0	0
Salts	(lb/10^6 Btu)	0	0	0	0
Metals	(lb/10^6 Btu)	0	0	0	0
Pesticides	(lb/10^6 Btu)	0	0	0	0
Air pollution					
NO_x	(lb/10^6 Btu)	0	0	0	0.187
SO_x	(lb/10^6 Btu)	0	0	0	0.22
H_2S	(lb/10^6 Btu)	0	0	0	Neg.
Particulates	(lb/10^6 Btu)	0	0	0	Neg.
Pesticides	(lb/10^6 Btu)	0	0	0	0
Solid waste total	(lb/10^6 Btu)	0	0	0	Neg.

[a] Basis: Cattle manure collected on 5-month cycle with liquid recycle.

TABLE B-11. ANAEROBIC DIGESTION[a]
(Case 2)

Impact		Resource extraction	Onsite processing or storage	Transport to conversion plant	Conversion plant
Land disruption and use	Acres/ 10^9 Btu/ day output	0	0	0	7.3 + 34 for evap. pond
Water pollution					
Input	(gal/10^6 Btu)	0	0	0	0[b]
Output	(gal/10^6 Btu)	0	0	0	0
Ammonia	(lb/10^6 Btu)	0	0	0	0
Phosphorus	(lb/10^6 Btu)	0	0	0	0
Salts	(lb/10^6 Btu)	0	0	0	0
Metals	(lb/10^6 Btu)	0	0	0	0
Pesticides	(lb/10^6 Btu)	0	0	0	0
Air pollution					
NO_x	(lb/10^6 Btu)	0	0	0	0.171
SO_x	(lb/10^6 Btu)	0	0	0	0.148
H_2S	(lb/10^6 Btu)	0	0	0	Neg.
Particulates	(lb/10^6 Btu)	0	0	0	Neg.
Pesticides	(lb/10^6 Btu)	0	0	0	0
Solid waste total	(lb/10^6 Btu)	0	0	0	Neg.

[a] Basis: Fresh cattle manure and wheat residue with liquid recycle.

[b] All wastewater goes to evaporation pond.

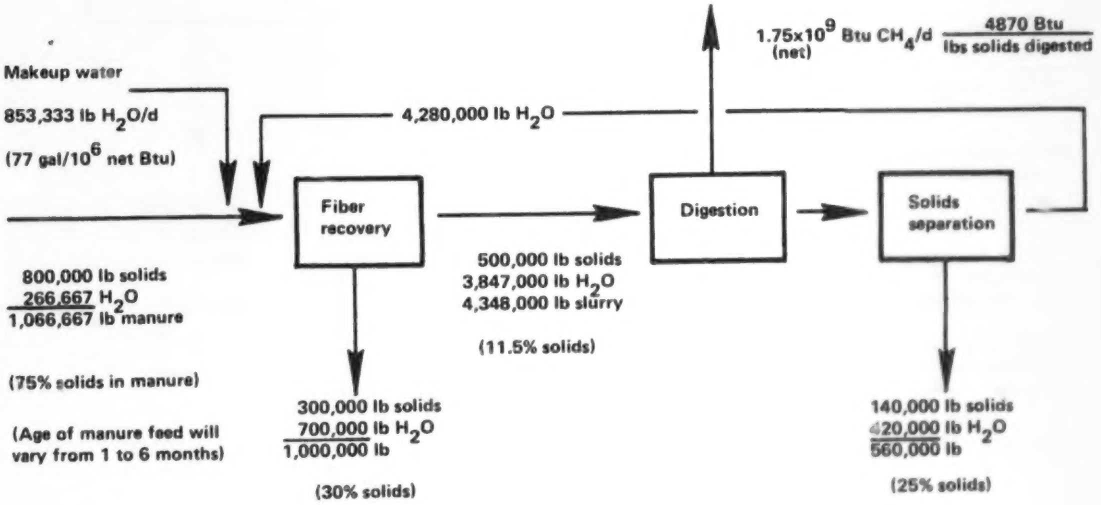
TABLE B-12. ANAEROBIC DIGESTION[a]
(Case 3-B)

Impact		Resource extraction	Onsite processing or storage	Transport to conversion plant	Conversion plant
Land disruption and use	Acres/ 10^9 Btu/ day output	0	0	0	42.2
Water pollution					
Input	(gal/10^6 Btu)	0	0	0	626
Output	(gal/10^6 Btu)	0	0	0	0
Ammonia	(lb/10^6 Btu)	0	0	0	0
Phosphorus	(lb/10^6 Btu)	0	0	0	0
Salts	(lb/10^6 Btu)	0	0	0	0
Metals	(lb/10^6 Btu)	0	0	0	0
Pesticides	(lb/10^6 Btu)	0	0	0	0
Air pollution					
NO_x	(lb/10^6 Btu)	0	0	0	1.87
SO_x	(lb/10^6 Btu)	0	0	0	0.90
H_2S	(lb/10^6 Btu)	0	0	0	Neg.
Particulates	(lb/10^6 Btu)	0	0	0	Neg.
Pesticides	(lb/10^6 Btu)	0	0	0	0
Solid waste total	(lb/10^6 Btu)	0	0	0	Neg.

[a] Basis: Fresh chicken manure with liquid recycle.

APPENDIX C

DATA COMPARISON FOR BIO-GAS, CRAP, AND SRI MODEL CASES



Water Balance
(No liquid discharge for this example)

Input		Output	
With manure	266,667 lb/day	With fiber solids	700,000 lb/day
Makeup water	853,333 lb/day	With digested solids	420,000 lb/day
	1,120,000 lb/day		1,120,000 lb/day

Solids Disposition

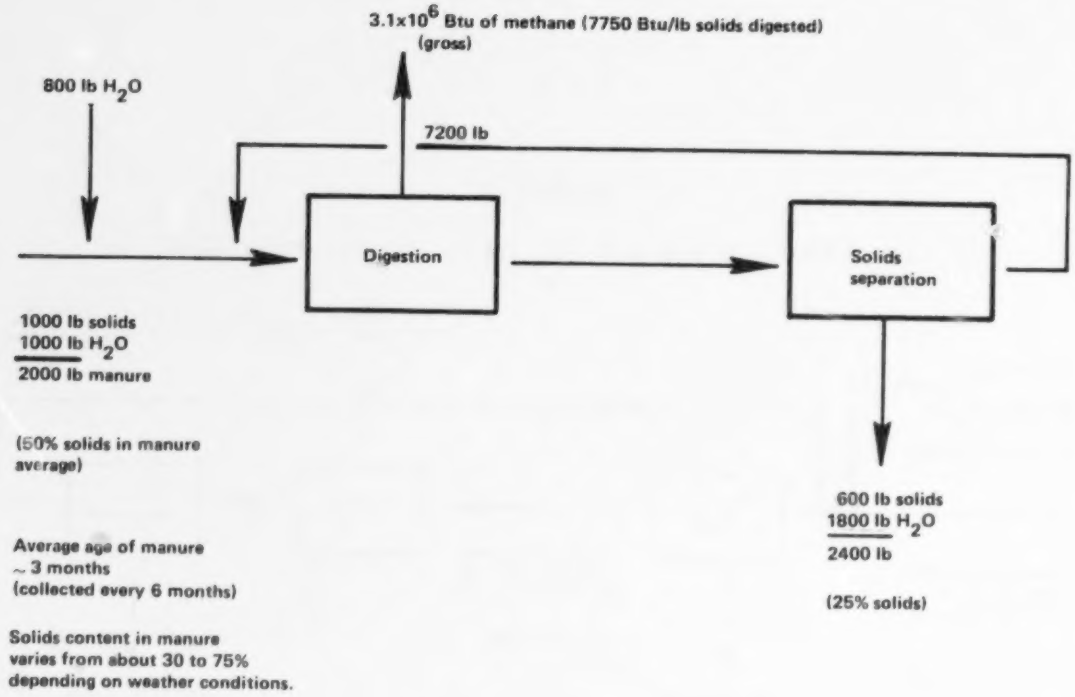
Input 800,000 lb/day
Output 440,000 lb/day

360,000 lb/day digested or 45% of input with a net CH_4 yield of about 1.753×10^6 scf or 4870 Btu/lb solids digested

Note: It was indicated that an evaporative pond would be provided for storm water runoff and any liquid purge stream. We assume purge stream might be required if manure moisture content is higher than for the case indicated in the example.

[a] Source: Personal communication with Mr. Chester Brooks of Oklahoma City, Oklahoma representing CRAP in September 1976. (Informed that no published information is available.)

Figure C-1. CRAP system mass balance.[a]


3.1x10^6 Btu of methane (7750 Btu/lb solids digested)
(gross)
800 lb H2O
7200 lb
Digestion
Solids separation
1000 lb solids
1000 lb H2O
2000 lb manure
(50% solids in manure average)
Average age of manure ~ 3 months (collected every 6 months)
Solids content in manure varies from about 30 to 75% depending on weather conditions.
600 lb solids
1800 lb H2O
2400 lb
(25% solids)

[a] Sources: References 28 and 29.

Figure C-2. Bio-Gas Inc. system mass balance.[a]

TABLE C-1. COMPARISON OF PARAMETERS USED BY BIO-GAS, INC. AND SRI FOR CATTLE MANURE

	Bio-Gas, Inc.	SRI	
		Manure, fresh	Manure, 5-month collection cycle
G	0.99	1.0	0.91
f_d	0.45 to 0.60	0.67	0.31
f_v	0.65	0.78	0.67
Total N in manure (dry basis)	3.7%	1.9%	2.5%
Total N in digester effluent (dry basis)	2.8%	4.1%	3.3%
θ_c, days	16.2	20	20
$\frac{\text{Volatile solids loading}}{\text{digester volume}}$	$\frac{0.52\text{x}10^6 \text{ lb vs}^a}{2.6\text{x}10^6 \text{ ft}^3}$	$\frac{1.72\text{x}10^6 \text{ lb vs}^a}{7.0\text{x}10^6 \text{ ft}^3}$	$\frac{1.47\text{x}10^6 \text{ lb vs}^a}{4.53\text{x}10^6 \text{ ft}^3}$
(lb vs^a/ft^3	= 0.20	= 0.25	= 0.32

[a] vs = volatile solids

TABLE C-2. COMPARISON OF SELECTED PARAMETERS FOR BIO-GAS, INC., CRAP, AND SRI MODEL CASES

	Bio-Gas	CRAP	SRI
Feed solids to digester, %	8	11.5	7 to 10
Solids content in feed solids, %	50 average (30 to 75 range)	75 (highest solids content)	20 to 50[a]
Gas output/lb of volatile solids converted, expressed in Btu/lb	7750 to 8800 (gross)	4870 (net)	5682 (net)
	Coal-fired heaters for digester		6553[b] (gross)

[a] Solids content of fresh cattle manure and urine would be approximately 15%. For the case of "fresh manure," assume 20% solids (case 1-A).

For Case 1-B, assume an average manure solids content of 50%.

For Case 2, assume that the moisture content is 27% and for cases 3-A and 3-B, 50%.

[b] Case 1-A with fresh manure.

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